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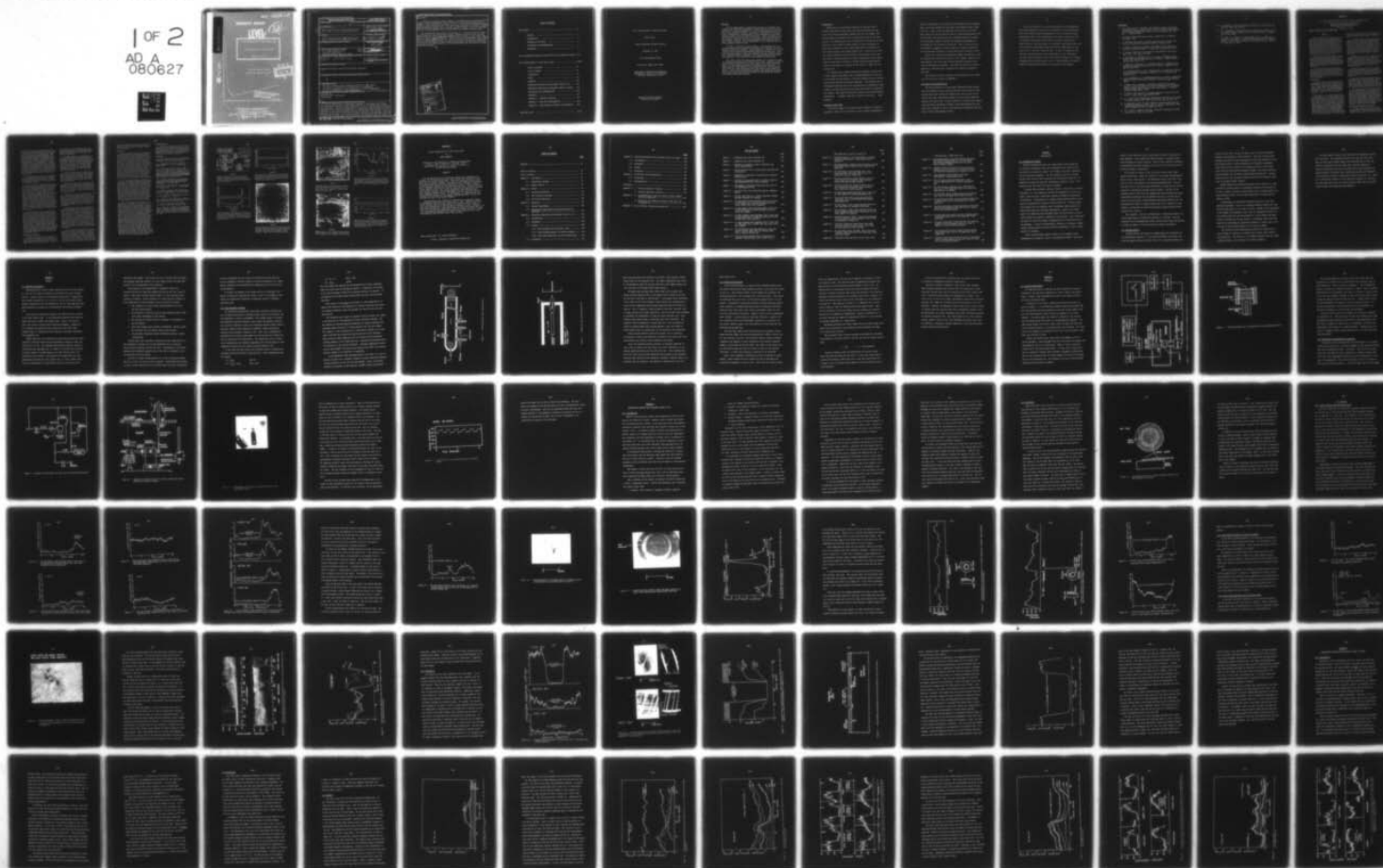
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USE OF KNOBLECTIONS TO STUDY SOLID FILMS

Ernest Rabinowicz and Mark Connolly

December 31, 1979

U.S. Army Research Office

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(6) Use of exoelectrons to study solid films.		(9) Final report,
7. AUTHOR(s)		6. PERFORMING ORG. REPORT NUMBER
(10) Ernest/Rabinowicz Mark/Connelly		8. CONTRACT OR GRANT NUMBER(s)
		(15) DAAG 29-77-C-0044
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
		(12) 113
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		(11) 31 Dec 79
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
(18) ARD (19) 15224.1-E		15. SECURITY CLASS. (of this report)
		Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Exoelectrons Friction Wear Lubrication Solid films		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
Two new applications of exoelectron emission to tribology were studied, both involving non-metallic films (which emit few or no exoelectrons) on metallic substrates. The first application dealt with hard, wear-resistant coatings. Experiments were conducted to determine if exoelectrons could be used as a new technique to help detect premature defects and localized film failure. Plots of emission versus location could then be used to determine coating quality and the wear process involved. The second application was concerned with soft, organic coatings and the measurement of their wear-out and possible migration along a		

wear track.

In order to facilitate these studies, a new apparatus was constructed which allows the sliding experiment to be carried out in the exoelectron-detection chamber. Thus, exoelectron emission, as well as friction can be measured continuously during the sliding test. This new testing procedure is much more flexible than the previous method, which involved frequent removals of the test specimen from the friction apparatus to the exoelectron test chamber and back again.

The results show that exoelectron emission is an excellent means of determining localized film failure due to wear. However, trying to find localized defects such as cracks proved to be quite difficult which, in turn, made evaluations of coating quality difficult. Results from the "simultaneous" tests showed that the lower pressures used ( $10^{-5}$  torr) did not greatly alter the exoelectron emission behavior. Solid films incorporating graphite and molybdenum disulfide were found to wear monotonically, while some migration was observed with Teflon-containing coatings.

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Use of exoelectrons to study solid films

Final report

Ernest Rabinowicz and Mark Connelly

December 31, 1979

U.S. Army Research Office

Contract No. DAAG 29-77-C-0044

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### Abstract

Two new applications of exoelectron emission to tribology were studied, both involving non-metallic films (which emit few or no exoelectrons) on metallic substrates. The first application dealt with hard, wear-resistant coatings. Experiments were conducted to determine if exoelectrons could be used as a new technique to help detect premature defects and localized film failure. Plots of emission versus location could then be used to determine coating quality and the wear process involved. The second application was concerned with soft, organic coatings and the measurement of their wear-out and possible migration along a track.

In order to facilitate these studies, a new apparatus was constructed which allows the sliding experiment to be carried out in the exoelectron-detection chamber. Thus, exoelectron emission as well as friction can be measured continuously during the sliding test. This new testing procedure is much more flexible than the previous method, which involved frequent removals of the test specimen from the friction apparatus to the exoelectron test chamber and back again.

The results show that exoelectron emission is an excellent means of determining localized film failure due to wear. However, trying to find localized defects such as cracks proved to be quite difficult which, in turn, made evaluations of coating quality difficult. Results from the "simultaneous" tests showed that the lower pressures used ( $10^{-5}$  torr) did not greatly alter the exoelectron emission behavior. Solid films incorporating graphite and molybdenum disulfide were found to wear monotonically, while some migration was observed with Teflon-containing coatings.



### Introduction

Exoelectrons, the spontaneous emission of electrons from a freshly formed metal surface, was first discovered many years ago (1,2) and has been extensively studied since (see for example 3-10). Unfortunately, few practical uses of exoelectrons have yet been discovered. One promising use is in the detection of cracks and the monitoring of crack growth in metals subject to cyclic stressing, in which case exoelectrons can be effectively used to investigate the pre-failure stages of the fatigue process (11). This led us to carry out a study during the years 1974-1977 on the possible uses of exoelectrons to study the process of surface fatigue wear, which constitutes the main mode of failure of rolling element bearings, and the results of this work are available in the forms of a paper (12) and a report (13).

The assembly of an exoelectron detection apparatus proved to be a rather complex undertaking, and it seemed appropriate, at the end of the surface fatigue study, to find other possible uses for exoelectrons and the exoelectron detection apparatus. One possible use, of tribological interest, was in the investigation of non-metallic films on metal surfaces, and the way that these films would be removed during sliding. This report contains the results of that investigation, initiated by Donald M. Boyd and, carried out mainly by Mark Connelly.

### Progress of the study

The initial stages of this study used a geometry as similar as possible to that used in the earlier surface fatigue investigation.

One ball, coated with a solid film, was slid against three stationary balls in the same geometry as that used in the familiar Shell 4-ball test (14). Later, a flat was machined on the surface of the ball, and a single pin was slid over the flat in a pin-on-disk geometry (15). In both cases, the sliding tests were conducted outside the exoelectron measurement chamber, and then the specimens were brought into the chamber for the exoelectron detection. Some of this early work is presented in Appendix A, which consists of a paper presented at the International Conference on Solid Lubrication in Denver in 1978.

Finally, the exoelectron measurement chamber was modified so that the sliding tests could be carried out in the chamber, using a pin on disk geometry, and at the same time the exoelectron emission rate could be monitored continuously. This work is presented in detail in Appendix B, constituting Mr. Connelly's M.S. Thesis, presented in May, 1979.

Work carried out by Mr. Connelly in the period after the completion of his thesis is given in Appendix C.

#### Discussion and Recommendations

The work carried out in this project demonstrates that exoelectrons can indeed be used to study non-metallic solid films and their wearing away, since exoelectron emission will start as soon as the film is worn away. Exoelectron emission can also detect flaws and cracks in the solid film. Of great interest is the fact that exoelectrons can detect situations in which a solid film migrates over the wear track, although in fact we only detected such migration with one type of film, namely baked-on Teflon.



One of the features of our work, and indeed of much contemporary work with exoelectrons, is that it is carried out in a vacuum environment, thus ensuring a direct measurement of the electrons and a good signal/noise ratio. The disadvantage of this type of testing is that it relegates exoelectrons to the role of an exotic research tool, rather than as a practical diagnostic technique. Many people think that this situation is inevitable, that exoelectrons simply cannot be measured in air. But this is not the case. In fact, it should be realized that exoelectrons were first discovered in an air environment, and some modern researchers, also, have worked in ambient air, although presumably with a poorer signal (16, 17). The development of improved methods of measuring exoelectrons in air would be very welcome.

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## Appendix A

### USE OF EXOELECTRON EMISSION IN THE STUDY OF SOLID LUBRICANT FAILURE

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#### Abstract

Solid films based on molybdenum disulfide and polytetrafluoroethylene were coated on steel balls, and sliding experiments were carried out in a laboratory atmosphere using a 4-ball tester and a pin-on-disk apparatus. The friction was measured continuously and the photo-stimulated exoelectron emission rate was monitored periodically. It was found that a rise in the photo-stimulated exoelectron emission rate, indicating wear-through of the lubricant-layer and the exposure of bare metal, correlated well with a rise in the measured friction coefficient, both indicating the same failure point for the lubricant film.

Localized film failure was studied using single point contact friction tests. In these tests a high photo-stimulated exoelectron emission rate was found at the same locations in the wear track where spikes indicating high friction were observed, and optical microscope observations confirmed that in these locations damage of the coated solid film lubricants had occurred.

It is considered that the exoelectron emission technique is especially suited to the evaluation of solid film lubricants in practical sliding systems, in which case friction measurements are generally not feasible. The exoelectrons help indicate when the solid film has worn through, and locate the site where this has occurred.

#### INTRODUCTION

As is well known solid film lubricants are effectively used in numerous sliding situations because they provide low friction and low wear over a wide range of ambient conditions. However they have one fundamental limitation, namely that it is almost impossible to replenish a solid lubricant film. Hence, they have a finite life and, after they are worn away, tribological failure generally ensues.

Accordingly, in studying a system lubricated by a solid film the most important question is generally that of determining the life of the lubricant film, which means measuring the point in time at which the film is worn away. The most common technique used to study solid films is that of measuring the friction coefficient of the sliding system. Generally, when a solid film lubricant is applied and sliding commences, the friction coefficient is at first reasonably low, and then generally drops a little further as sliding continues. At this point the friction stabilizes, and remains constant as the film is gradually worn away. Then towards the end of the useful life of the film the coefficient of friction gener-

ally rises, and then some cut-off friction coefficient value (e.g. 0.4) is generally taken to denote complete wearing away of lubricant (1).

This method is quite satisfactory in practice, but it does have one major disadvantage; namely it cannot be applied to practical engineering systems in which monitoring of the friction is impossible or inconvenient. Also, it does not deal well with a number of situations in which the friction coefficient is a function of lubricant film thickness. This paper describes a new method for the detection of solid film lubricant breakdown. This new method consists of monitoring the photostimulated exoelectron emission (PSEE) from the wear track.

Exoelectrons are electrons (typically with energies of the order of 1 e.v.) which are emitted from a surface which has been freshly formed by a process such as abrasion (2), phase transformation (3), plastic deformation (4) or fatigue cracking (5). The emission rate is initially high, but then decays with time (6) with a half-life which is often of the order of an hour.

Obviously, the energy which the emitted electron possesses must come from somewhere, and various researchers have debated the relative importance of the two most obvious energy sources, namely the re-arrangement of surface atoms and oxidation or other chemical processes (7).

The natural exoelectron emission rate is generally low, but it may be greatly increased by illuminating the emitting surface with ultra-violet light. The ultraviolet light confers an important advantage; by moving the light beam relative to the surface it is possible to examine the exoelectron emission rate from various locations on the surface (4), (5).

The experimental technique used in this case consists of applying to the metal surface a solid lubricant film of a material which emits no exoelectrons or at any rate a small number. Molybdenum disulfide and teflon, in both cases in resin binders, have proved very suitable for this purpose. Initially, after these films are applied to a metal, there is negligible emission from the lubricated surface. If the surface is now exposed to sliding conditions, wear of the solid lubricant occurs and as the substrate becomes exposed, the emission of exoelectrons is initiated.

#### APPARATUS AND EXPERIMENTAL PROCEDURE

The PSEE detection apparatus has three primary systems, which have been described in some detail (8). The first system is the PSEE detection chamber which uses a mercury diffu-

sion pump to obtain a pressure of  $10^{-5}$  torr. Second, there is the detection system which uses a focused ultraviolet (UV) light spot to stimulate the emission of the exoelectrons. Electrons are detected by an electron multiplier and counted by an electronic ratemeter. The output from the ratemeter is displayed on the Y axis of an X-Y recorder. The third system of the apparatus is for locating the spot on the specimen which is to be irradiated. A ferrofluidic rotary vacuum feedthrough, coupled to a digitally controlled stepping motor, controls the position of the specimen. The rotary feedthrough is initially at the starting point and the signal corresponding to the rotational position is read on the X axis of the X-Y recorder. A schematic illustration of the apparatus is shown in figure 1. The output from a test is a plot of exoelectron counting rate versus angular position.

Two modifications were made to the apparatus. First an ultraviolet filter was added to lower the background counting rate. Second, the resolutions of the PSEE detection apparatus was improved by making the UV light spot smaller (.03 mm x 1.15 mm).

For the solid film lubricant described in this paper, a four ball testing rig was used in which the three lower balls were rigidly fixed in a cup by solidified Woods metal. The top ball was pressed against the three balls by a dead weight load, the lower three balls were rotated, and a strain gage torque meter was used to measure the torque produced in the top ball. From this measurement, the mean friction coefficient could be readily computed. To apply a solid lubricant film, the top ball was abraded in a ball mill, cleaned in an ultrasonic chlorofluorocarbon bath and coated with the solid lubricant, either a  $\text{MoS}_2$ -resin combination or a Teflon-resin film. The coating was allowed to cure for 24 hours before testing was started. All test balls were 52100 steel of diameter 12.7 mm. All the tests were run dry, in air. The normal force on the top ball was 30 N. The speed of rotation of the bottom balls was 40 rpm.

Before the first test, the coated test specimen was placed in the PSEE detection apparatus and a scan was made showing PSEE counting rate versus distance along the wear track. The test specimen was then positioned in the four ball rig and a sliding test was initiated. Friction measurements were made continuously during the test. At various intervals the four ball rig was stopped, the coated top ball was removed to the counting chamber, and a PSEE scan was made. Photomicrographs were made at locations along the wear track in which PSEE peaks were present. Then the ball was replaced in the friction apparatus, and sliding was continued. The test was run until the coefficient of friction rapidly increased indicating that the lubricant had failed. This procedure was used for all tests.

#### RESULTS AND DISCUSSION

Figure 2 shows a plot of the coefficient of friction ( $f$ ) and PSEE rate in counts per minute versus the number of revolutions for the  $\text{MoS}_2$ -based film, while the figure 3 shows the same data for the Teflon-based film. The fric-

tion plotted is the averaged value for the three contact points in the four ball testing rig over one revolution, and the PSEE value plotted in figures 2 and 3 is also the mean value for each scan.

As figure 2 shows, the coefficient of friction for the  $\text{MoS}_2$  was initially high (0.4) and stabilized at 0.2 after ten revolutions. After 800 revolutions  $f$  began to increase significantly. The value of PSEE initially shows a variation in counting rate and stabilizes after ten revolutions. An increase in PSEE begins at 800 revolutions. The PSEE scans after each run in the four ball rig showed variations in emission rate along the wear track during the first ten revolutions and after 500 revolutions.

Figure 3 indicates that the PTFE coating shows a low value of friction coefficient and of PSEE until 7000 revolutions. Both  $f$  and PSEE increased after 7000 revolutions indicating a failure of the lubricant. The individual scans made during the PTFE test showed little variation along the wear track in the PSEE counting rate.

Of great interest in the matching of the appearance of the surface with the exoelectron emission rate. Figure 4 shows the appearance of the Teflon-coated surface after only a few cycles of sliding, at a place where exoelectron emission is a minimum. It will be seen that the lubricant layer is spread out evenly along the sliding track.

Figures 5 and 6 show the appearance of the  $\text{MoS}_2$  film after 1100 revolutions. At this point much of the film has been worn through. Figure 5 shows the point of lowest PSEE, and it will be seen that a partial film still covers the surface. Figure 6 is of a region of maximum PSEE, and the lubricant film is almost completely worn away. Figure 7 shows the positions on the track at which the micrographs were taken.

It was found that the 4-ball tester had one great disadvantage when an attempt was made to match peaks in the friction and in the PSEE, since the friction coefficient at any point of time is the mean of the friction at three separate locations. Accordingly, tests were carried out in a modified pin-on-disk tester in which a single 52100 steel pin was slid against a steel surface coated with Teflon, the position of the pin being arranged in such a way as to produce a wear track of the same diameter as in the four ball test. (By keeping the diameter of the wear track constant we were able to eliminate adjustment of the optical system). In this case the force on the pin was 50 N and the rotational speed was 40 rpm.

Figure 8 shows a comparison between the friction and PSEE values during one cycle of rotation. It will be seen that, in general, peaks in the friction and peaks in the PSEE rate tend to coincide. In fact, the correlation coefficient between the two variables is 0.40, (on a scale in which 1 denotes perfect correlation and zero denotes no correlation). A correlation coefficient of 0.40 is a reasonably high positive correlation. No doubt the



correlation would have been better but for the fact that exoelectron emission rates are a function of time as well as amount of metal at the interface.

#### DISCUSSION

The above experiments have shown that the technique of exoelectron emission monitoring provides a powerful tool for studying solid film lubricants. First, by studying the overall exoelectron emission rate we can get a good indication of the state of the solid film, since the counting rate is low as long as the solid film is coherent, but rises rapidly as the film is worn through. Second, by studying exoelectron emission from specific locations we can study localized film failure, with the advantage of being able to examine a large area of solid film in a relatively short time. Third, it seems likely that exoelectrons can be used to study more sophisticated phenomena, such as the transport of solid film lubricant material along the wear track. Some evidence was obtained that a region, from which the solid film was removed at an early stage of sliding, could be covered by a lubricant at a later stage, but the evidence is not definitive.

All in all, the exoelectron monitoring method has considerable advantages over present techniques for studying solid film lubricants, which generally utilize friction coefficient measurements. Exoelectron measurements do not have to be made during a wear test, which has some advantages. They can be used either to define average conditions over the whole wear track, or else to give specific information about particular locations on the wear track. The main limitations appear to be first that the substrate material should undergo PSEE readily, which requirement excludes polymers and ceramic oxides; and second that the solid lubricant film should not be a strong emitter of exoelectrons, which requirement excludes soft metal lubricants like lead and indium.

One of the reviewers of this paper has pointed out that exoelectron emission is just a research tool, and that it appears to be as cumbersome to use as the SEM, which, with analytical attachments, might give more information about films and wear. In terms of our paper this is a very valid point, but in terms of long-range potential it is seriously misleading. Exoelectrons can be measured in air as well as in vacuum, using either a specially modified Geiger counter (9) or a microammeter which detects ionization induced by the exoelectrons (10). Thus, exoelectrons can be used to periodically monitor large solid-film lubricated surfaces which are part of an operating mechanism whereas there is often no non-destructive procedure for getting such surfaces into an SEM. Two further advantages of exoelectrons. First, since they are only emitted from those regions of the surface from which the solid lubricant film has been removed, they automatically attract attention to the regions most likely to be of interest. Second, the cost of an exoelectron detection system is likely to be appreciably less, perhaps by a factor of three, than that of an SEM. In any case, we thank the reviewer for his thought-provoking comment.

#### ACKNOWLEDGEMENTS

This work was carried out under contract DAAG 29-77-C-0044 sponsored by the U.S. Army Research Office - Durham, and the authors wish to thank Edward A. Saibel of that office for advice and assistance. One of the authors (N. Ohmae) was the recipient of a Murata scholarship while this work was carried out.

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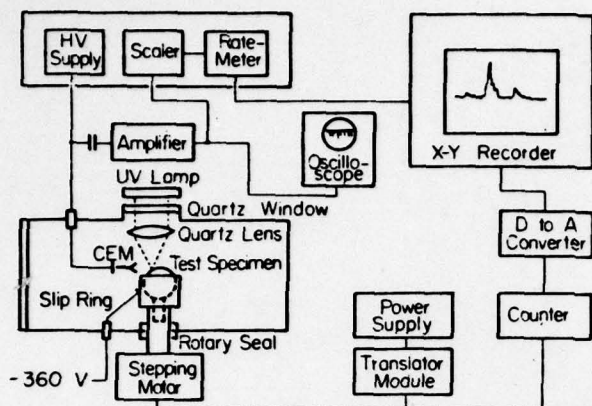


Figure 1

Schematic illustration of the exoelectron detection apparatus, showing the detection chamber on the left, the counting circuitry on the top, and the controls for positioning the ball at the bottom.

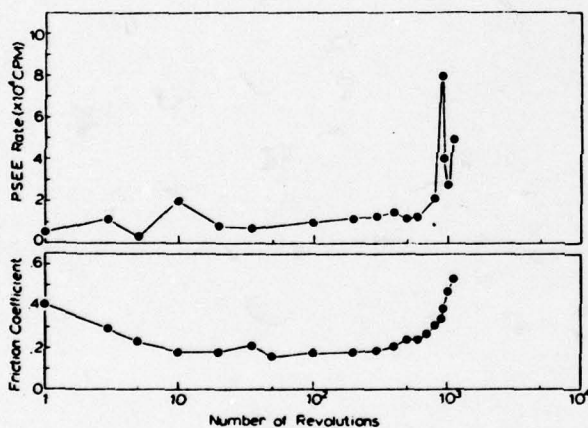


Figure 2

Electron emission rate (top figure) and friction coefficient (bottom figure) as a function of number of revolutions using one steel ball lubricated by a  $\text{MoS}_2$ -resin film and sliding on three other steel balls. Load 3 kg, sliding speed 15 mm/sec.

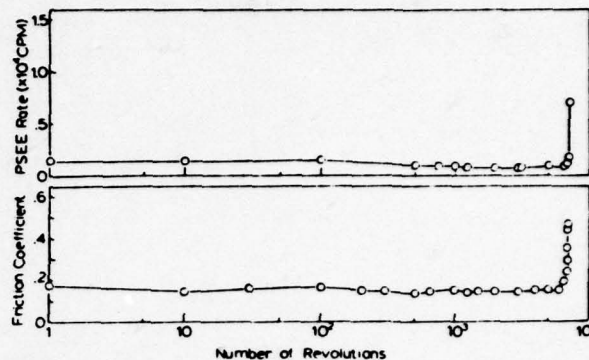


Figure 3

Electron emission rate (top figure) and friction coefficient (bottom figure) as a function of number of revolutions using one steel ball lubricated by a Teflon-resin film and sliding on three other steel balls.

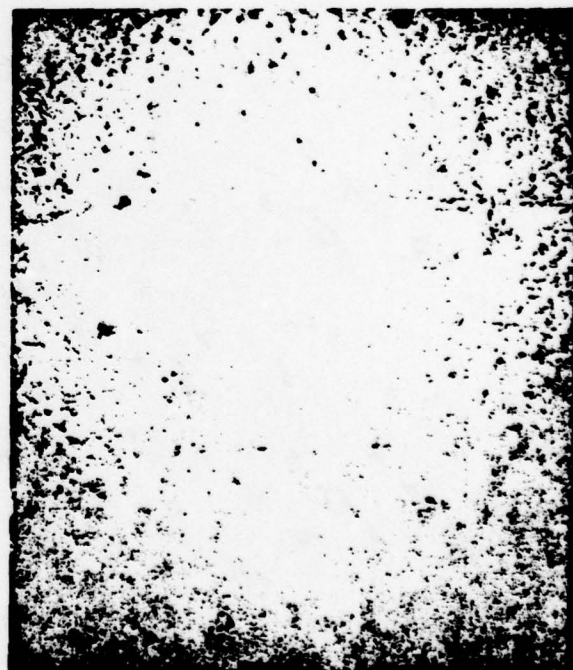


Figure 4

Photomicrograph of steel ball covered by a Teflon film after 100 cycles, at a place where the exoelectron emission was a minimum. Magnification x60. Note that the lubricant layer is coherent. Load 3 kg, sliding speed 15 mm/sec.





Figure 5

Photomicrograph of a ball covered by a  $\text{MoS}_2$ -resin film, after 1100 revolutions, at a location where electron emission is a minimum. Magnification x60. Some film is still to be seen in the wear track.



Figure 6

Same as figure 5, but a location where the exoelectron emission is a maximum. At this location, no film is to be found in the wear track.

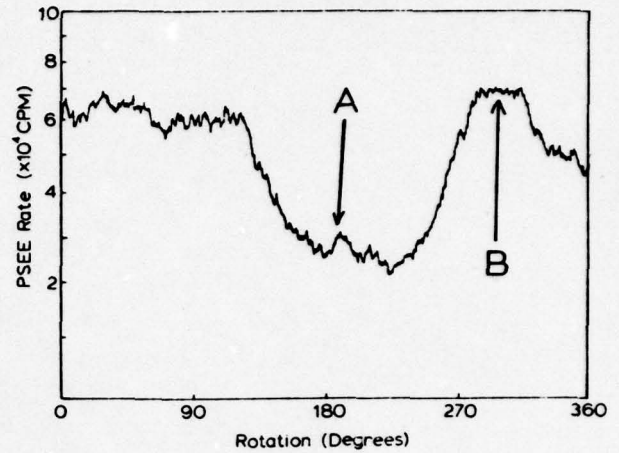


Figure 7

Exoelectron emission as a function of position along the wear track for a steel ball covered with a  $\text{MoS}_2$ -resin film, after sliding for 1100 revolutions. The locations A and B from which figures 5 and 6 were photographed are indicated.

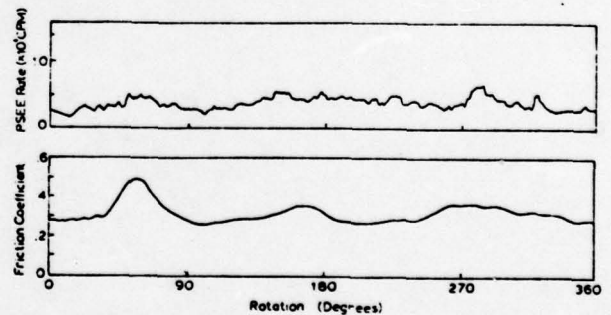


Figure 8

PSEE and friction as a function of angular position for steel disk lubricated by a Teflon-resin film, on which a steel pin has slid for 3240 revolutions. Note that high spots on the two traces tend to coincide, the correlation coefficient being 0.40.



## Appendix B

### USE OF EXOELECTRONS TO STUDY SOLID FILMS

by

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Submitted to the Department of Mechanical Engineering  
on May 1, 1979 in partial fulfillment of the  
requirements for the Degree of Master of Science in  
Mechanical Engineering

#### ABSTRACT

Two new applications of exoelectron emission to tribology were studied, both involving protective films (which emit little or no exoelectrons) on metallic substrates. The first application dealt with hard, wear-resistant coatings. Experiments were conducted to determine if exoelectrons, along with semi-destructive tests, could be used to detect premature defects and localized film failure. Plots of emission versus location could then be used to determine coating quality and the wear process involved. The second application was concerned with soft, organic coatings and the measurement of their wear-out and possible migration along a track. In this regard, an apparatus was constructed which enabled one to conduct simultaneous wear, friction and exoelectron tests in the vacuum chamber.

Results showed that exoelectron emission was an excellent means of determining localized film failure due to wear. However, trying to locate defects such as cracks proved to be quite difficult which, in turn, made evaluations of coating quality dubious at best. Results from the "simultaneous" tests showed that the lower pressures used ( $10^{-5}$  torr) did not alter the exoelectron emission behavior too much. Graphite and molybdenum disulfide were found to wear monotonically, while some migration was observed with Teflon coatings.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Introductory Remarks

Without coatings and films, life today would be very different. Our aircraft, automotive, steel and innumerable other industries all rely heavily on protective layers for thermal, electrical, corrosive, and even decorative purposes. Two very important types of coatings include those used for wear resistance and lubrication, especially as demands for energy and materials conservation continue to grow. This research deals with these two types of coatings.

A typical wear resistant coating is either a hard oxide or carbide. Obviously, it is very important for both the manufacturer and the customer to know how well a particular coating is capable of protecting the substrate. Unfortunately, no single non-destructive method is adequate for evaluating the quality of these films (21). The two inspection methods that are presently used to determine coating quality are visual observation and thickness measurements. However, the former tends to be subjective and unreliable while the latter does not necessarily reflect the quality or adhesion of the coating. Also, these methods cannot be used with complex configurations or on parts with internal passages. It would be advantageous, therefore, to develop a method whereby coating quality could be quantified regardless of size, configuration or thickness.

Solid film lubricants usually consist of soft organic resins impregnated with graphite, Teflon or molybdenum disulfide. Once pene-

tration to the substrate occurs, catastrophic failure of the part becomes imminent. Also, unlike hard oxide coatings, in practice solid film lubricants are rarely repaired. There is much interest, therefore, in determining how these coatings wear out and if the time and point of penetration might be predictable.

Our research is unique in the tool used to study these films, namely exoelectrons. These are electrons of low energy "spontaneously" emitted from a fresh surface. The phenomenon usually lasts but a few hours (in air) with emission rate decreasing exponentially. The Surface Lab at M.I.T. has been using exoelectrons to study various surface properties, particularly rolling contact fatigue. The bulk of the equipment used in this study was designed and tested several years ago. An excellent description of the apparatus and how it was used can be found in the two theses, "Photostimulated Exoelectron Emission for the Non-destructive Study of Surface Fatigue Wear," by P. March (17), and "Effect of a Lubricant on Exoelectron Emission during Rolling Contact Fatigue" by D. Boyd (3).

This research - the use of exoelectrons to study solid films, is a further application of exoelectron emission to tribology. With the exception of the aforementioned theses, previous work using exoelectrons to study any aspect of the wear process is almost non-existent.

### 1.2 Present Efforts

Initial efforts were devoted to demonstrating the feasibility of the experimental approach. It was known beforehand, that oxide, carbide and organic materials emitted little or no exoelectrons when dis-



turbed, whereas fresh surfaces of metals such as steel and aluminum produced large amounts of these electrons. With this in mind, metal specimens covered with these non-metallic layers were subjected to wear and grinding tests of various durations in a laboratory atmosphere. These would then be followed by an exoelectron scan of the surface. Cracks and worn spots which penetrated through to the metal substrate, would presumably be indicated by high exoelectron emission. Coating quality and the wear processes involved could then be evaluated using plots of emission versus location.

Results showed that exoelectron emission (also referred to as EE) provided an excellent means of determining localized film failure due to wear. However, trying to locate defects such as cracks proved to be quite difficult which, in turn, made evaluations of coating quality dubious at best.

As mentioned, the exoelectron emission process is a very time dependent phenomenon - the rate of emission decaying rapidly with time and being much faster in air than in vacuum. Because of this dependency, it was thought that scanning a wear track for exoelectrons within fifteen seconds after the pin had traversed it, would improve the application of exoelectrons in wear studies. Accordingly, much effort was devoted to constructing the apparatus necessary to conduct wear, friction and EE tests simultaneously in the evacuated chamber.

The results of these simultaneous wear/EE tests showed that we were fortunate to operate in a medium vacuum (rather than a high or ultra-high one). The effects of a low oxygen pressure were not a major problem although it did influence the results somewhat.

The major aspect of these tests dealt with the migration of solid film lubricants. One unanswered question was, does the first spot where the base metal becomes exposed, grow monotonically or does the lubricant repeatedly cover the naked spot, then get removed etc. Because exoelectrons have very low energy and are easily stopped, any organic material introduced onto a fresh metal surface would "absorb" these electrons and cause a significant decrease in the EE rate. Therefore, exoelectrons seemed to be one sensitive technique for locating, not only those spots where the coating had worn away, but also any new areas to which the coating may have migrated.

## CHAPTER 2

### REVIEW

#### 2.1 Exoelectron Emission

Exoelectrons are a fairly recent discovery which hold much promise as a tool in the study of materials, their defects and their eventual failure. Several reviews of the emission process and its applications have recently appeared (3, 13, 17, 18, 27, 28, 29) and General Motors Research Laboratories was even prompted to take out full page advertisements extolling its virtues as an accelerated life testing technique (19).

The history of exoelectrons began in the 1920's with the creation of the first Geiger tubes. It was universally observed that brand new tubes would give a higher than normal count. After a few hours or days, this erratic counting would eventually disappear. Apparently, this "anomaly" was ignored by most people until the 1940's when Johannes Kramer, a German physicist, decided to seriously investigate the phenomenon (27).

Kramer found that any fresh metal surface emitted electrons "spontaneously," and that these electrons possessed an energy of about one electron volt (1 eV). His findings puzzled many scientists because it contradicted the knowledge that, to remove an electron from a surface, a definite amount of energy (known as the work function) had to be delivered to that surface. The question then became where do these spontaneous electrons get their energy from. At first, Kramer attributed this phenomenon to an exothermal reaction, and thus the term



exoelectron was dubbed. This theory was later rejected, even by Kramer, and although sometimes referred to as the Kramer effect, the name "exo-electron" is now ensconced in the literature.

Unfortunately, even though Kramer's exothermic theory was rejected, this did not mean that someone had come up with the "correct" theory. Even today, several theories exist as to how and why an exoelectron is emitted. Current theories (3) (some being very similar to those expounded for other phenomena, such as corrosion) include:

1. The formation of a dipole layer during adsorption of water onto the fresh surface.
2. The formation of electron traps in semi-conducting metal oxide layer after deformation of the surface.
3. The creation of vacancy sites for oxidation or adsorption on the new surface.
4. Slip steps formed during (plastic) deformation having a lower work function than the thicker oxide coated surface.
5. The increased roughening during deformation causing a change in photoyield.

Shortly after their discovery, exoelectrons were being hailed as a new measurement technique for surface phenomena such as corrosion, metal cutting, grinding, friction and wear. Unfortunately, the initial euphoria has diminished primarily due to the lack of consensus on how an exoelectron gets its energy.

At first, it might seem paradoxical to use EE in material studies when one is still not sure how they originate. Nevertheless the process is such a surface sensitive one, and enough cause and effect information

has been formulated over the years, that exoelectrons have been successfully employed in several studies of material degradation as a diagnostic, analytical and non-destructive examination tool (2,7,11,14,15, 16,18,23,29,34).

Of course, the purpose of this study was not to investigate the nature of exoelectron emission but rather to use it and attempt to determine its engineering feasibility in different areas of tribology - especially wear.

## 2.2 Wear Resistant Coatings

In tribological applications, hard (wear resistant) coatings protect by simply preventing or delaying contact between the substrate and the atmosphere or service environment. The enormous range of coatings and application methods available, often leaves the engineer confused. For a metallic substrate, some of the available methods include electrophoresis, chemical vapor deposition, plasma-arc flame spraying and detonation gun spraying to mention a few. Cost, size, configuration, repairability and service environment all help dictate one's choice for how the coating will be administered. The coating must also be chemically, mechanically and thermally compatible with the base metal so that undesirable stresses are not induced in either material (21).

In our work with hard films, four different types of coatings were purchased from Union Carbide's Linde Division. Their compositions were as follows:

- |  |             |
|--|-------------|
| (1) $\text{Al}_2\text{O}_3$                | (99+ %)     |
| (2) $\text{Al}_2\text{O}_3 + \text{TiO}_2$ | (60% + 40%) |

- |                                    |             |
|------------------------------------|-------------|
| (3) WC + Co                        | (87% + 13%) |
| (4) Cr <sub>2</sub> O <sub>3</sub> | (99+%)      |

The first three were applied via the detonation gun (D-gun) technique while the fourth used the plasma-arc method. In addition, one coating of the Norton Company's Rokide ZS (zirconium silicate) was studied. It was applied by the simple flame spray process and had a nickel-chrome undercoat.

Even though we tested all the coatings in a wear application, in general the oxides are used primarily for thermal insulation and protection against oxidation, while the carbides are used for wear and seal applications.

The detonation gun (D-gun) is patented by Union Carbide (see figure 1) specifically for the application of wear resistant coatings. The gun operates by metering measured quantities of oxygen, acetylene and suspended powder particles of coating material into the gun chamber. This mixture is then detonated with a timed spark, sending a hot, high speed (1700 mph) gas stream with molten particles at the workpiece. These particles imbed themselves into the surface where microscopic welding produces a very strong bond (25). Successive detonations build the coating up to the desired thickness. Although temperatures within the gun reach 6000°F, the plated part remains below 300°F and therefore physical damage to the substrate is negligible.

In the plasma-arc flame spraying process (see figure 2), a gas or mixture of gases (e.g. nitrogen, hydrogen or argon) along with powdered coating materials are fed into the gun chamber. There, an internal electric arc produces a high velocity, 30,000°F plasma stream which



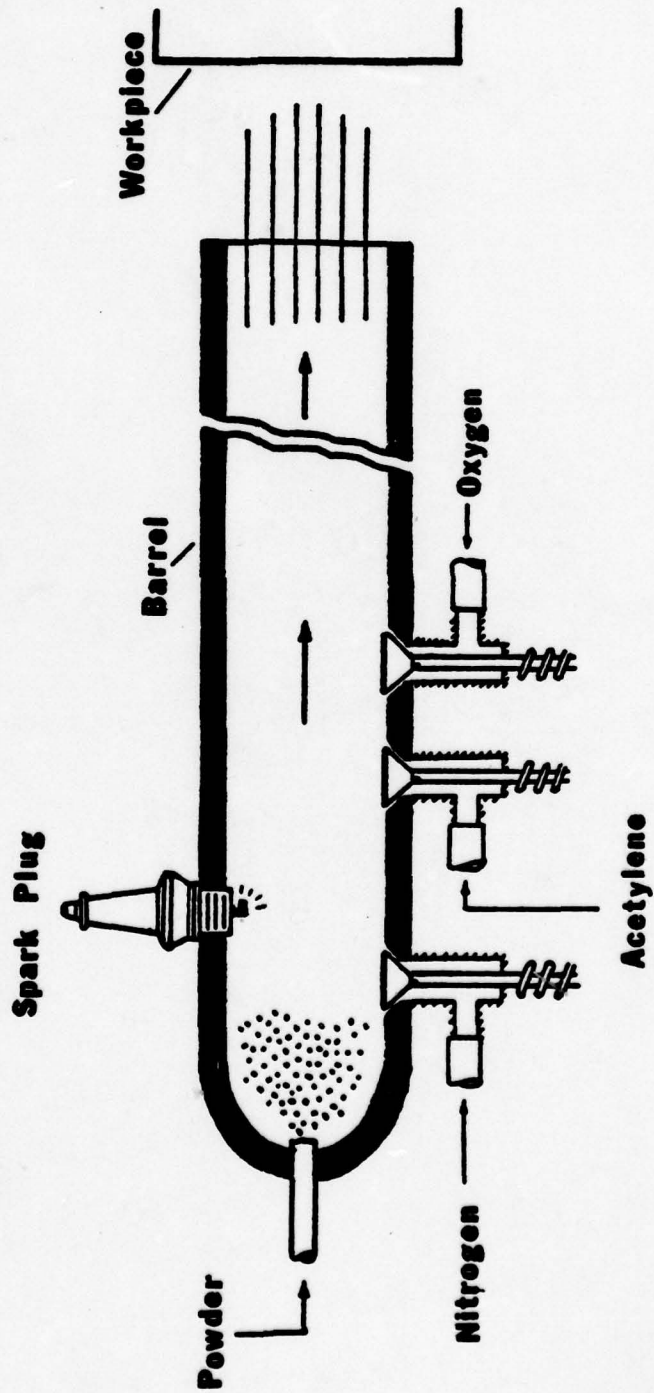


Figure 1 - Detonation gun (from reference 25).

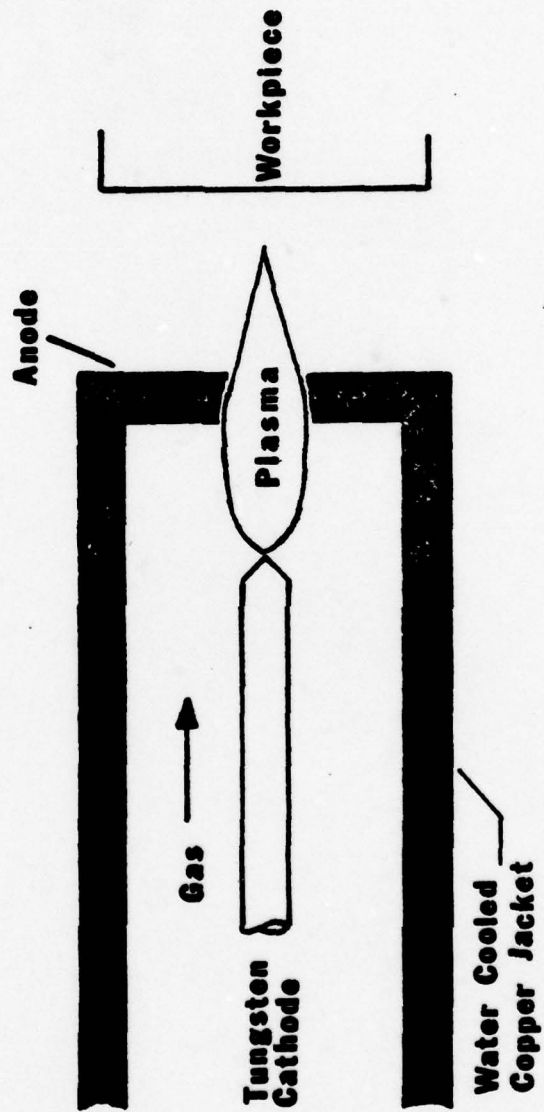


Figure 2 - Plasma-arc gun (from reference 25).



melts and accelerates the particles to produce a high density, closely bonded layer on the workpiece (25). The higher temperature heat source of the plasma-arc gives the coating particles a much higher energy content than that of the simple flame spray process.

Detonation gun coatings have a much higher bond strength than plasma coatings primarily due to the higher kinetic energy of the powder particles (1700 mph vs. 300-700 mph). Accordingly, metal substrates to be coated by the D-gun technique rarely require any sandblasting or other surface roughening whereas plasma deposited materials almost always do. Also, in general a D-gun coating is more wear resistant than a plasma coating of the same composition. Very few studies have attempted to determine the mechanism(s) of wear for these materials (32) - most research being devoted only to determine their wear resistance. One exception would be Mendelson's recent work (20). For his particular system (a plasma sprayed  $\text{TiO}_2$  coating against a cast iron rider) he found several forms of coating wear, all of which were load dependent.

These included adhesive interaction between the two surfaces, intergranular fracture and subsurface cracking of the coating and three body abrasive wear owing to oxide formation and removal.

Since the substrate-coating interface is extremely important to this study, we should note that there is no clear consensus as to the bonding mechanism between the two materials (33). Three explanations which are often cited include mechanical interlocking of the roughened surfaces (most especially for plasma-arc coatings), chemical reaction or alloying with the substrate, and adhesion or cohesion due to Van der

Waals forces (32).

### 2.3 Solid Film Lubricants

A solid film lubricant is a material which separates moving surfaces (most often metals) under boundary conditions and reduces the amount of wear (4). They usually consist of fine powders with inherent lubricating properties, that are mixed with a resinous binder. They should be considered when one or more of the following conditions (9, 10) are present: inaccessible lubricating locations, extreme operating temperatures, exposure to contaminating particulates, intermittent operation, operation after long static time, and/or environments which are reactive with conventional lubricants. However, some of their disadvantages (8,9) include: a finite amount of available lubricant, a higher friction coefficient than with hydrodynamic lubrication, a necessity for wear debris removal, higher cost, and inability to carry away any heat generated during operation.

The three most common solid film lubricants are graphite, molybdenum disulfide ( $\text{MoS}_2$ ) and polytetrafluoroethylene (PTFE or Teflon) and our work involved all three. Two different types of Teflon (a Dupont trademark) were applied to steel substrates by the American Durafilm Company - Teflon TFE and Teflon-S #550. The former is used chiefly for its anti-stick properties while the latter is used for its abrasion resistance. A third Teflon coating is referred to as Teflon-HD.

Teflon can be applied to substrates by either sintering or resin-bonding. Resin bonded films are normally applied by spraying with conventional equipment or aerosol cans. Since they are cured at relat-

ively low temperatures, they can also be applied to substrates of plastic, rubber or wood. The sintered films are deposited as aqueous dispersions onto the solid surface and then allowed to dry in air. The dried surface is then heated so that the particles soften and sinter leaving a continuous film with many tiny pores adhering to the substrate. Subsequent coating operations will eliminate these pores - however, too thick a coating may cause cracks in the film similar to the cracking of dried mud (9). When applied to metals, it is important that the surface be clean but that the normal surface oxide remain intact. Adhesion is increased if the real surface area is increased and therefore most parts are roughened by sandblasting. Specific information as to how these coatings are applied is generally difficult to obtain because the process supposedly is a trade secret.

Molybdenum disulfide was either rubbed into the surface using loose powder or was "painted" on using Acheson Colloid's Molydag 232 ( $\text{MoS}_2$  in an alkyd resin solution).

The frictional force on these coatings is determined by the shearing strength of the solid film (S), and the real area of contact and the load:

$$f = \frac{S}{P} \quad , \quad P \equiv \text{yield pressure}$$

Teflon is unique in that its coefficient of friction is only about one-third the value of this ratio. In fact, the coefficient of friction for Teflon is lower than that of any other known solid (9). A value of 0.04 is usually quoted against steel with values as low as 0.016 reported.



Friction coefficients for purified  $\text{MoS}_2$  can range from 0.03 to 0.12 merely by changing the method of application.

The wear of Teflon is similar to that of most other polymers. Under sliding conditions thin films of TFE are transferred to other (uncoated) surfaces such that in actuality one has TFE sliding on TFE (6,9). Briscoe and Tabor report two mechanisms of transfer - thin film (10 nm - 50 nm) at low loads, intermediate temperatures and smooth surfaces, and "lumpy" or relatively thick film transfer (0.1-1.0  $\mu\text{m}$ ) otherwise. However, the adhesion of these films to the "clean" surface is usually quite poor and the films fail by mechanical removal of the microscopically thin layers generating wear debris consisting primarily of lubricant particles (22). The "sharp edges" of the other sliding surface, shears a layer of the film (sometimes the entire film) from the substrate. Eventually, dynamic stability is lost and the metallic contact surfaces gall and seize.

### CHAPTER 3

#### APPARATUS

##### 3.1 General Improvements

The apparatus used to stimulate and detect exoelectron emission consisted of the same basic components as found in Boyd's and March's theses. However, some refinements were made to the system and these will now be elaborated upon.

A schematic of the overall stimulation and detection system is shown in figure 3. A new linear/log ratemeter (Baird Atomic model 980-435) was purchased and used primarily as the high voltage supply while the old scalar/ratemeter (model 125-B) was employed in its former capacity. The oscilloscope (see figure 1, reference 3) was deleted from the system except when used in a trouble-shooting capacity. The same vacuum system, 9-54 filter, quartz lens, UV light and CEM (Channeltron Electron Multiplier) which Boyd used, were retained. The resolution of the apparatus, determined by the size of the ultraviolet light spot, was 0.03 mm x 1.15 mm.

Several new fixtures were constructed to accommodate our flat, coated specimens. These specimens were all 11/16 inches in diameter and approximately 3/16 to 1/4 inches high. Figure 4 shows a cross sectional view of the positioning fixture. So long as the coated piece was not loosened or removed from the holder, alignment was maintained when it was reinserted into the vacuum chamber by virtue of the milled flat on the positioning rod. The opening at the top of these holding fixtures was 5/8 inches in diameter.

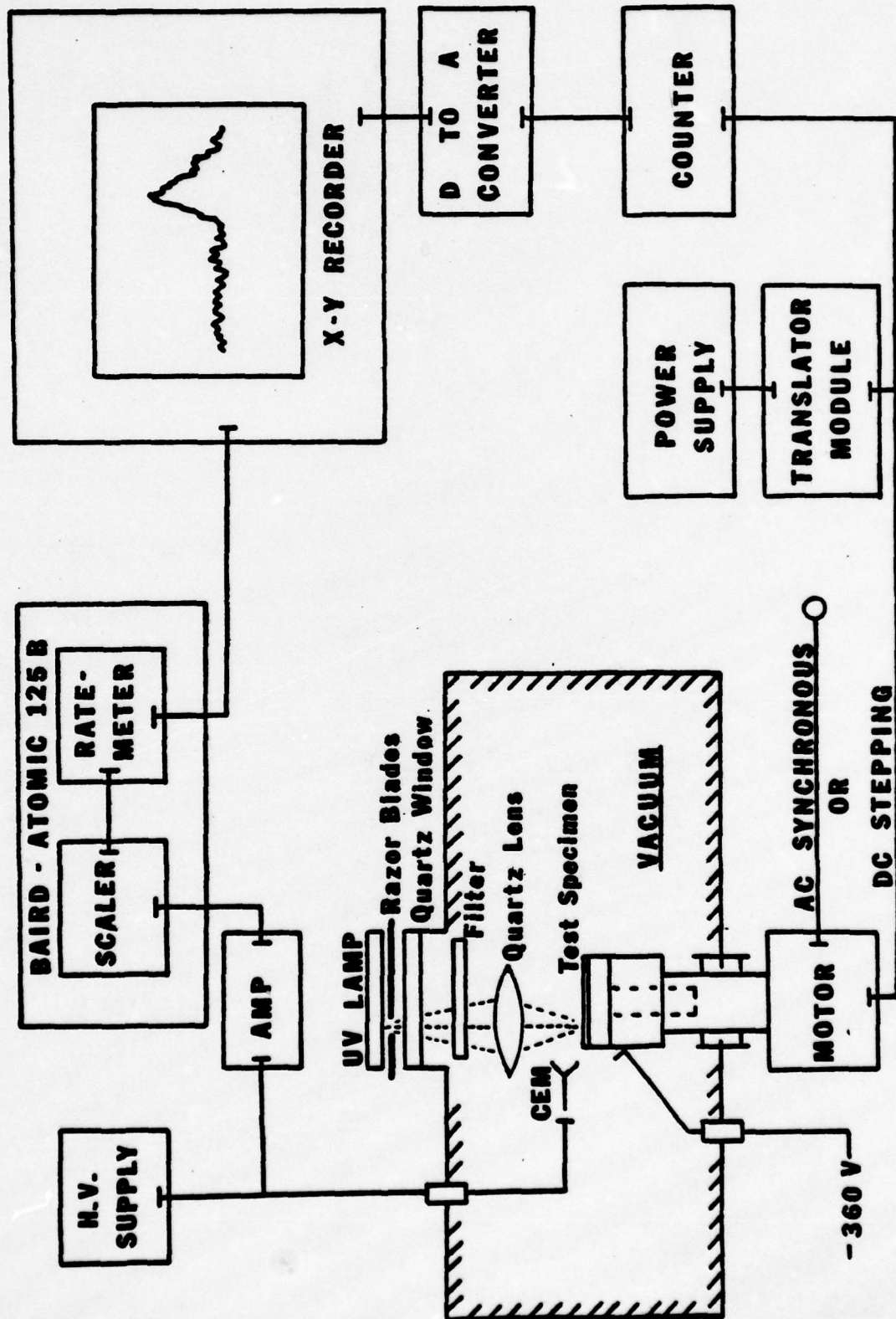


Figure 3 - Schematic of apparatus used to stimulate and detect exoelectrons.



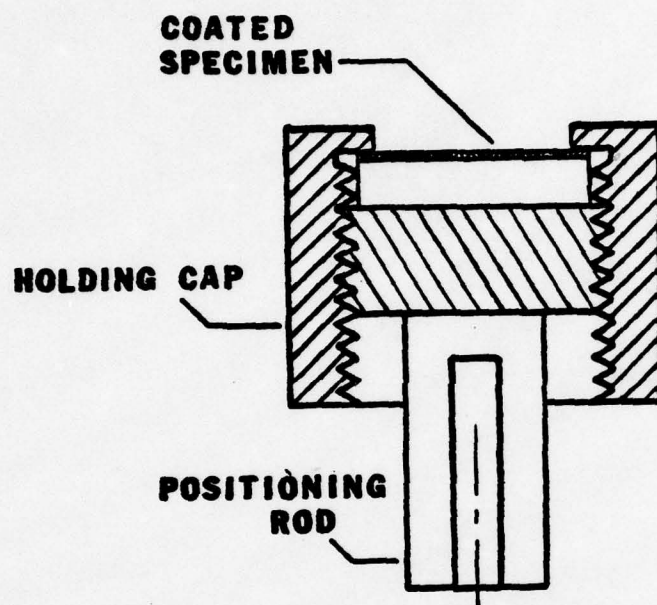


Figure 4 - Cross sectional view of coated piece and positioning fixture.

The previous amplifier circuitry, which often broke down, was replaced with a simpler circuit using eleven fewer resistors and two fewer amplifiers. These are shown in Appendix 1. The new amplifier proved to be much more reliable and easier to repair. Other electronic modifications to the apparatus (see figure 5) included a voltage divider for use with a digital voltmeter so that one was sure that the same voltage was applied across the CEM each time. A toggle switch, resistor and microammeter were added to the bias voltage circuitry. The resistor was added as a safety precaution and the microammeter was included to indicate if a short circuit had developed.

During the first half of this project, all tests were conducted in atmospheric air. Wear tests were run with the standard pin-on-disk configuration which generated circular wear tracks approximately one-half inch in diameter at loads of up to 2 kilograms. Friction force measurements were plotted on a Sanborn Recorder. Grinding tests were done on a "magnetic chuck" surface grinder with a 1/2 inch wide aluminum oxide wheel.

### 3.2 Simultaneous Wear/EE/Friction Apparatus

In contrast to the initial tests, the second phase of the project involved the construction of special equipment so that exoelectron emission could be monitored during wear tests. Since the electron detector used (the CEM) can only be operated in a vacuum of better than  $10^{-4}$  torr, these simultaneous tests also had to be conducted in a vacuum of this magnitude. The setup (see figures 6 and 7) is similar to the usual pin-on-disk geometry. A cantilever beam load cell (see Appen-

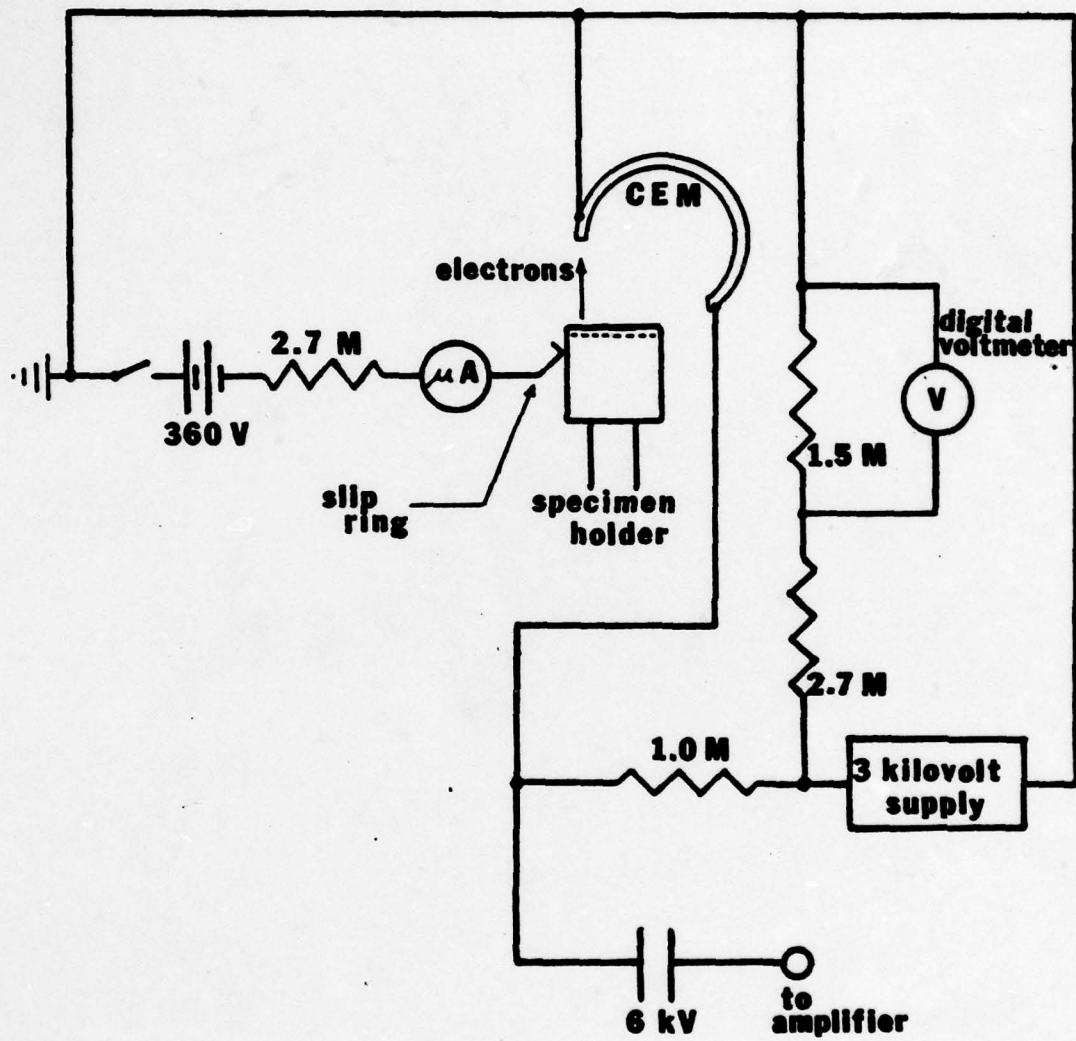


Figure 5 - Schematic of electronic circuitry used including modifications.



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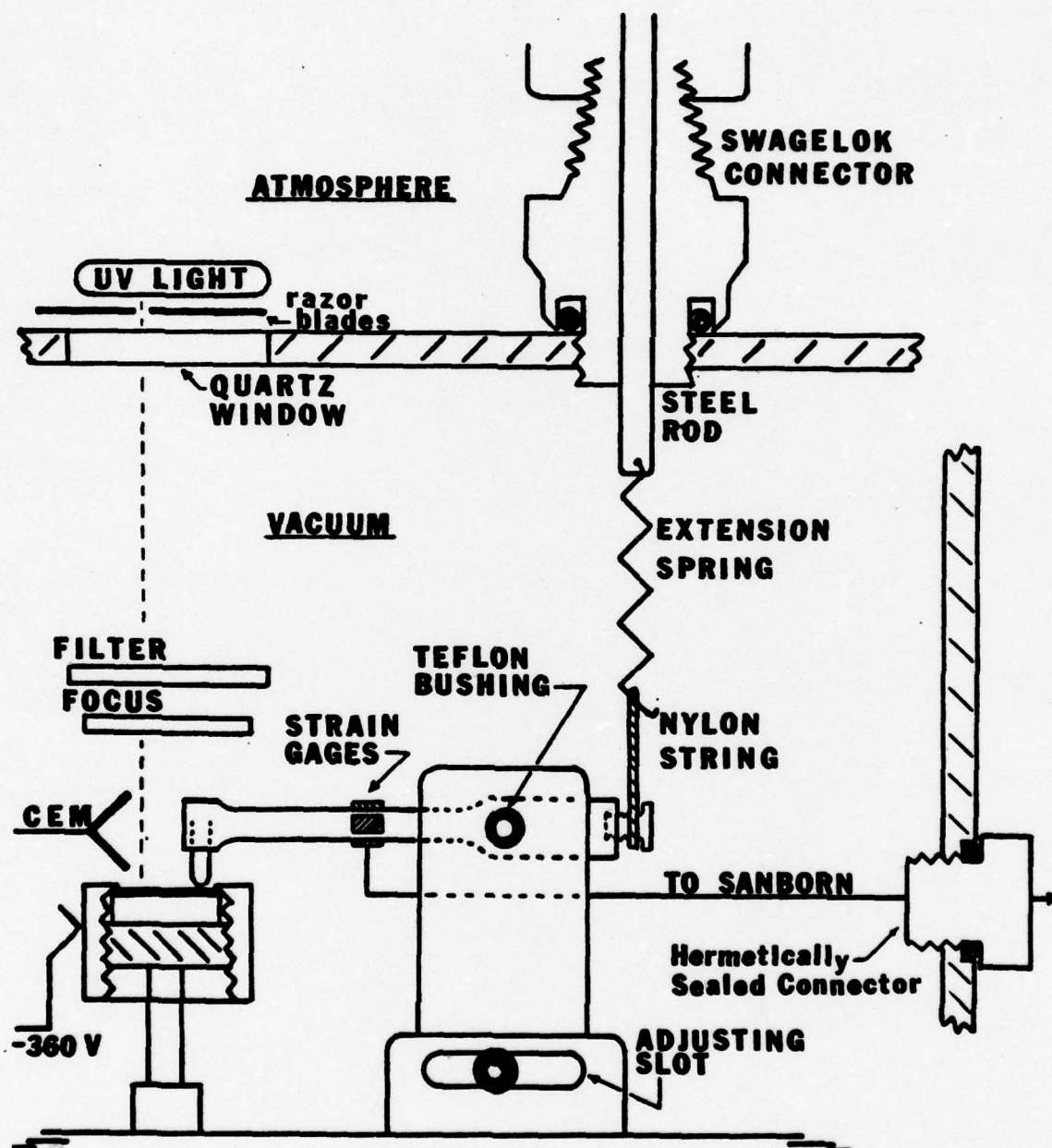


Figure 6 - Schematic of apparatus used to conduct simultaneous wear/EE/friction tests in vacuum.

-B27-

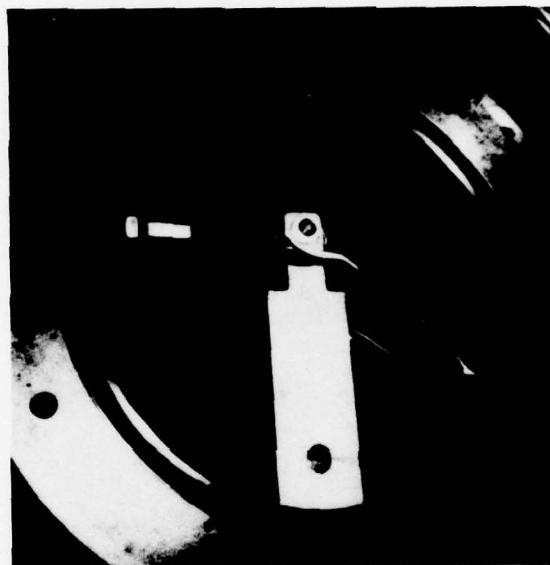


Figure 7 - Photograph of cantilever beam load cell used in the simultaneous tests.

dix) is employed due to space limitations. Both the friction and normal forces can then be measured and fed to a Sanborn recorder through an eight pin, hermetically sealed connector. The normal load is applied using an extension spring (with a spring constant of 3.3 kilograms per inch) attached to the "opposite" end of the armature. The pin and armature are electrically isolated from the rest of the chamber with two Teflon bushings about which the arm pivots, and a nylon string attached between the spring and the arm. This is necessary because the test specimen is negatively biased at 360 volts. The base of the wear tester is fixed to the floor of the vacuum chamber with Eastman 910 adhesive. An adjusting slot in the base allows the fixture to be moved in or out so that the wear track passes under the UV light spot, producing the desired photo-stimulated exoelectron emission (PSEE). A delay of 15 seconds is encountered between the time the pin traverses a certain spot and EE can be measured from that same location. This is because the place where the pin contacts the surface is approximately 90 degrees from where the UV light hits the surface. The Swagelok connector serves the dual purpose of holding the spring extended (producing the normal load) while at the same time maintaining the vacuum. The only drawback to this arrangement is that the load cannot be adjusted without having the chamber revert to atmospheric pressure.

Friction traces obtained when using the DC stepping motor (see figure 8) were meaningless because of the constant starting and stopping of the specimen. To alleviate this situation, two AC synchronous



### STEEL ON STEEL

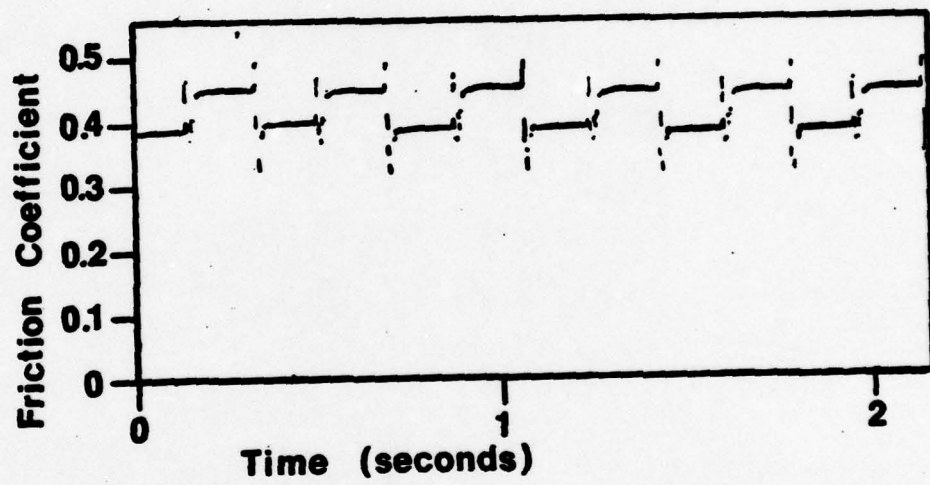


Figure 8 - Friction force trace obtained using DC stepping motor.

-B30-

motors with speeds of one and ten rpm's were purchased. The motor mount was changed so that both AC motors and the DC stepping motor could be easily interchanged. When the AC synchronous motor was used, the angular position of the specimen (x position) was plotted on the x-y recorder by letting the DC motor turn "in air" (unattached) or by operating the recorder in the test mode.

## CHAPTER 4

### EXOELECTRON EMISSION AND SPECIMENS TESTED IN AIR

#### 4.1 Introduction

March's rolling contact fatigue tests demonstrated that EE could predict the location of a spall. However, Boyd's further work showed that EE predictions were correct in only some cases since environmental conditions, especially the lubricant used, played a crucial role in the outcome (3,17). In addition, Baxter's success using exoelectrons to predict fatigue life stemmed partially from the fact that experiments were conducted with clean specimens in vacuum, with no contaminants to worry about (2). It was obvious that any further application of exoelectrons would have to be with relatively clean specimens since the emitted electrons possess very little energy and are easily stopped.

In tribological applications, coatings and films were a logical next step because they are generally used without any other material, such as a liquid lubricant, present. Therefore, with the possible exception of wear particles, they would not be subject to environmental contaminants.

The purpose of these tests was two fold - to study the wear process of films utilizing exoelectrons, and to see if semi-destructive tests along with EE might enable one to predict coating quality.

Wear is defined as the removal of material from solid surfaces as a result of mechanical action. Burwell and Rabinowicz have classified four types of wear (26):

1. Adhesive - the transfer of fragments formed by adhesive



forces of intimate contacting atoms.

2. Abrasive - the plowing of grooves by a rough, hard surface sliding on a softer one.
3. Corrosive - wear in the presence of corrosive environments.
4. Surface Fatigue - repeated sliding or rolling with loading and unloading causing surface and/or subsurface cracks which lead to large fragments.

Obviously, for the cases studied here, we may immediately rule out corrosive wear. Surface fatigue wear might be observed in the hard oxide and carbide coatings since, during repetitive sliding, brittle materials undergo a form of fracture which produces a series of cracks in the wear track. Two body abrasive wear will probably be observed whenever the pin is much harder than the specimen and three body abrasion may occur in the presence of hard coating wear particles. All other conditions will most likely lead to adhesive wear.

Is it possible to distinguish between these forms of wear using exoelectrons? Although we know that exoelectron emission is largely a function of the amount of new surface area created, the absence of an acceptable EE theory forces us to rely on empirical evidence. Also, we should recall that in this research it is the base metal, not the coating, which partakes in the Kramer effect. Finally, one must remember that we are only measuring the rate of emission (other parameters, such as the energy of the electrons, are not examined here). Therefore, our question becomes do different types of substrate wear produce different rates of EE.

It has already been noted in the literature (27) that more electrons are emitted at high sliding loads than at low ones due primarily to the greater surface area generated by the former. However, under similar conditions (i.e. load, speed, distance), different types of wear do not necessarily produce dissimilar amounts of surface area. Therefore, an alternative possibility might be to study the behavior of exoelectron emission with time for various forms of wear. Should either the decay or the rate of EE depend on the type of wear involved, our study of the wear process using exoelectrons will be greatly enhanced.

Regardless of the type of wear, however, it was believed that exoelectrons could be used to detect localized film failure in both hard oxide and soft organic coatings. Presently, the only method which is used in sliding situations is to measure the friction coefficient (visual observations usually require stopping and removing the part in question). The only problem with this method is that, in most engineering circumstances, measurement of friction forces is either difficult or impossible. Monitoring the wear track for EE seemed to be a viable alternative. There also was interest in determining if the friction and EE rate increased together or if one rose before the other. In the latter case, the one that increased first could be promoted as the better forecaster of film failure due to wear.

It was also proposed that the quality of wear resistant coatings be predicted using exoelectron emission. As previously mentioned, there is no single acceptable method to measure coating quality. A "semi-destructive" test which would propagate and/or widen already

weak areas (e.g. cracks) in the coating and continue on to form fresh surfaces in the base metal was, when used with EE, one possible remedy. Although our trial tests scanned only a small portion of the coating (a circular track of width equal to the length of the ultraviolet light spot), in practice a wear test could be conducted over the entire surface and, likewise, the entire coating would be scanned for EE in a raster pattern similar to that done by Veerman (34). From the plots of EE vs. position, the area beneath the curve would be calculated. A certain numerical value would then be chosen as the dividing line between acceptance or rejection of the coated part. In addition, should the emission exceed a certain value (e.g. 1000 cpm) at any one point, the piece would be considered defective.

Of course, this procedure could not be used with solid film lubricants because "cracks" and other defects in the coating would not be expected to continue through the harder base metal. However, even though no method was proposed to measure the quality of these soft coatings, the exoelectron emission process is ideally suited to studying their wear. It has been noted that most polymers wear by first transferring thin layers to the other surface, creating, in effect a polymer on polymer situation. This lead to the hypothesis that some solid film lubricants migrate along the track and that this migration could be noted by a corresponding decrease in the EE rate. The initial tests for migration were done in air. Later, more extensive tests were conducted in vacuum and these are discussed in the subsequent chapter.



#### 4.2 Procedures

Steel was chosen as the base metal for both hard wear resistant coatings and the soft organic films because of its relatively high emission of electrons when disturbed. Standard stock bars of 1095 and 1117 type steels were machined into disks of the necessary thickness and diameter. These were then sent out to be commercially coated as mentioned in Chapter 2. All coatings were purchased in two different thicknesses, 2 mils and 8 mils. The hard oxide and carbide materials were left "as coated," that is, no finishing or polishing was done to them. However, for some of the pin-on-disk tests, the hard coatings were partially ground by us at an angle so that the thickness varied, as shown in figure 9. In this manner the base metal would initially wear through in only one spot and the direction of wear would be uniform from that spot.

To start a test, the coated specimen is placed inside the positioning fixture (figure 4) which, in turn, is mounted in the pin-on-disk apparatus. The pin and armature are adjusted so that the wear track will conform to the UV light spot (or alternatively, the UV light spot can later be adjusted to pass over the wear track). The desired load is placed over the pin and the initial sliding speed is relatively fast (25 cm/sec) although friction force measurements are taken at much slower speeds (1 cm/sec). The wear test is stopped when the friction shows a marked increase, when the coating has visibly worn, or after the elapse of a certain time period. The fixture is then removed from the pin-on-disk setup and the specimen cleaned with freon degreaser and/or kimwipes (except in those cases where the effect of

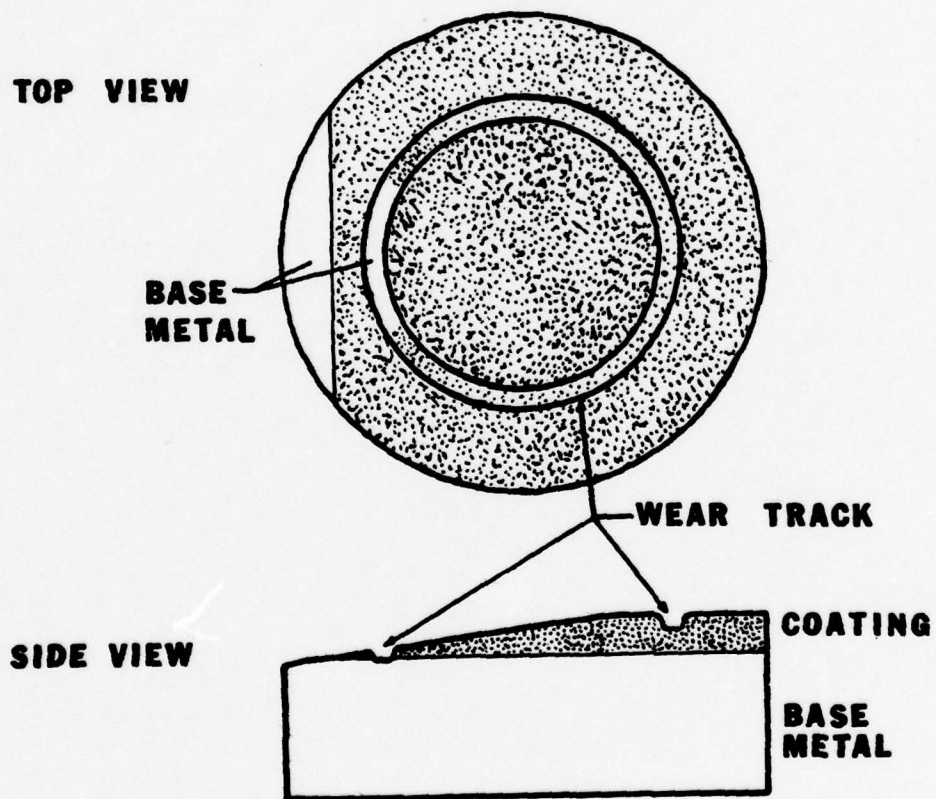


Figure 9 - Top and side views of a typical specimen showing varying thickness of coating.

any wear particles was of interest). After inserting the fixture into the EE chamber and assuring that everything is aligned properly, the system is pumped down to a typical pressure of  $10^{-5}$  torr. The time involved, from the end of a wear test to the beginning of an EE scan varied between five and ten minutes. Before running the actual scan, the specimen is positioned to zero, the voltage across the CEM is applied (checked via the digital voltmeter) and the bias voltage is switched on.

In addition to the pin-on-disk tests, other specimens were subjected to surface grinding. Since we were trying to create defects, no effort was made to grind 'properly' although the aluminum oxide grinding wheel was repeatedly dressed. No metallic particles were present in the wheel and very small amounts (0.5 mils) of coating were removed per test. The specimens had to be removed from the positioning fixture when placed on the magnetic chuck. In this case, realignment of the piece was assured by visual markings when it was placed back in the fixture.

Finally, in order to determine the effect of possible migrating films of Teflon on the exoelectron emission process, wear tests were conducted with uncoated specimens and steel pins. Pure Teflon would then be gently rubbed on 1/2 the wear track and an EE scan taken as before.



### 4.3 Results

#### 4.3.1 Hard Coatings and Pin-on-Disk Tests

Our first tests were run using steel specimens coated with zirconium silicate and a nickel-chrome undercoat (Norton Company's Rokide ZS, see appendix for properties). The thickness of the coating varied as shown in figure 9 and the pin used in the wear tests was a crystallon N silicon carbide material at a 500 gram load. Wear tests and abrasion with diamond showed that fresh coating surfaces had no tendency to emit exoelectrons and therefore it was assumed that coating wear particles did not "artificially" increase the exoelectron emission rate. The wear particles did interfere, however, with the EE scan by reducing the overall count where the underlying metal had worn through. In figures 10 and 11, one can see the difference between "dirty" and "clean" (using Freon TF degreaser) tests under otherwise identical circumstances. It is interesting to note that a similar test using a steel pin and a plain (uncoated) steel disk gave similar results (figures 12 and 13). Apparently, even metallic wear particles can reduce the EE rate.

Regrettably, we did not catch the first initial breakthrough in the coating because of a malfunctioning CEM. The first "accurate" EE scans took place a short time after a small portion of the metal substrate became exposed. A record of these EE plots, made during a 50 hour (not continuous) wear test at 500 grams, is shown in figure 14. The relatively flat portion (low emission) on the left side of each plot corresponds to the "still-coated" portion of the wear track, while the peaks, generally on the right side, correspond to those areas

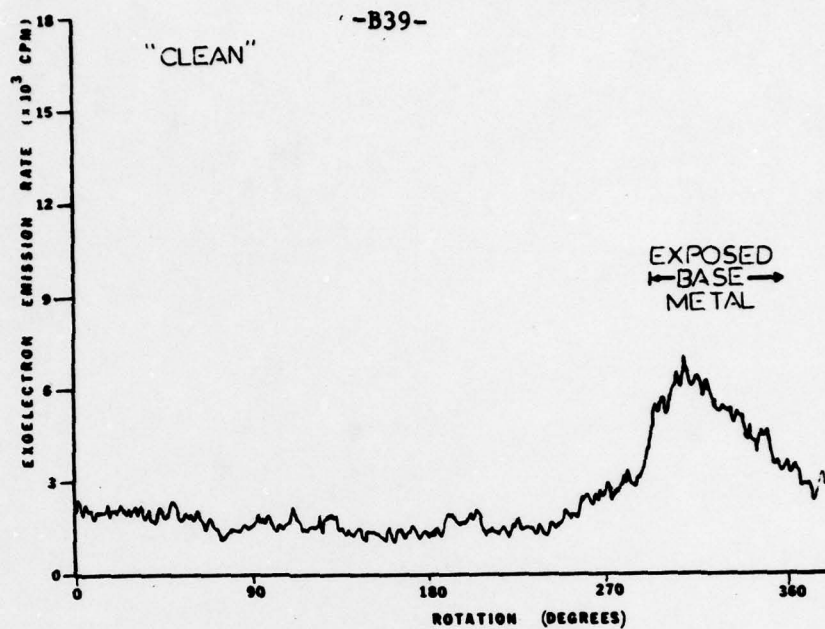


Figure 10 - EE from Rokide coated specimen after a wear test at 500 grams with a silicon carbide pin; wear track cleaned with Freon degreaser..

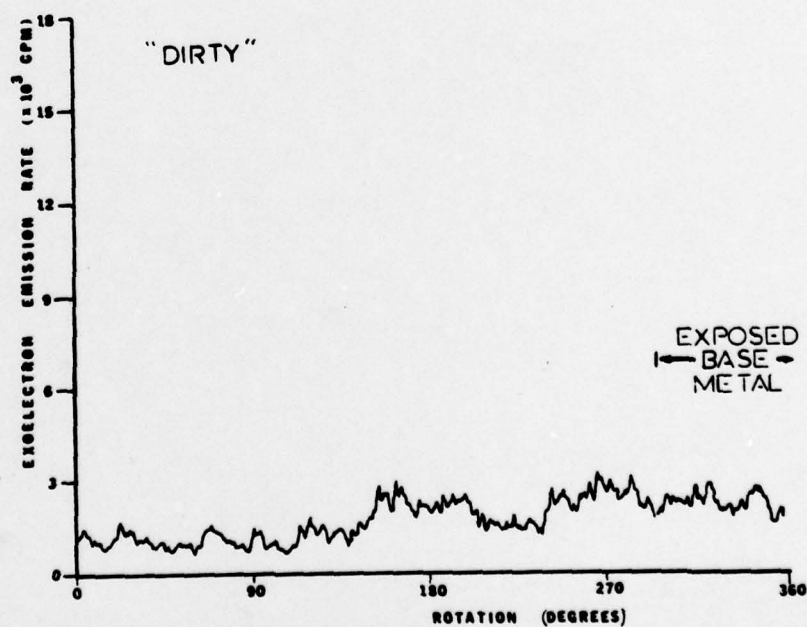


Figure 11 - EE from Rokide coated specimen after a wear test at 500 grams with a silicon carbide pin; wear track not cleaned.

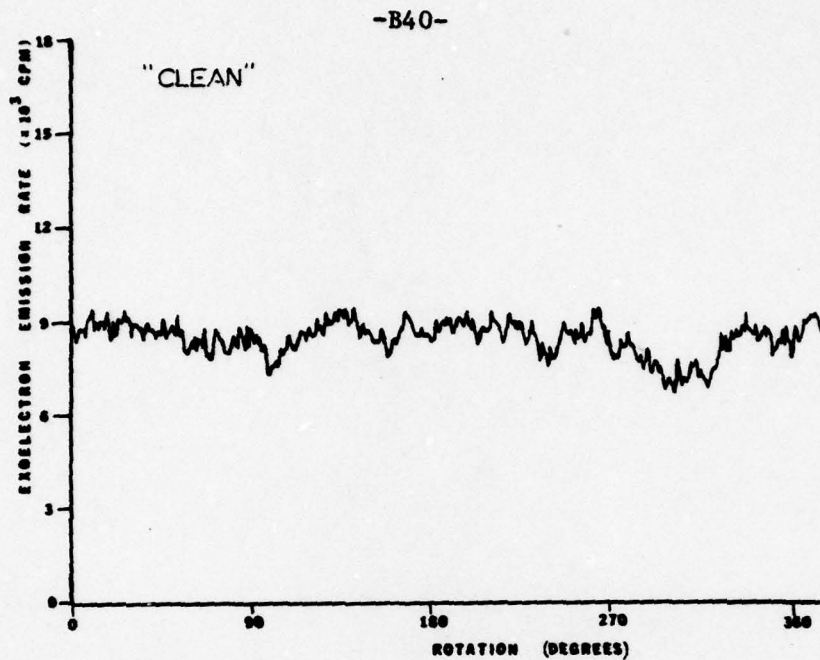


Figure 12 - EE from uncoated steel specimen after a wear test at 1000 grams with a 52100 steel pin; wear track cleaned with Freon degreaser.

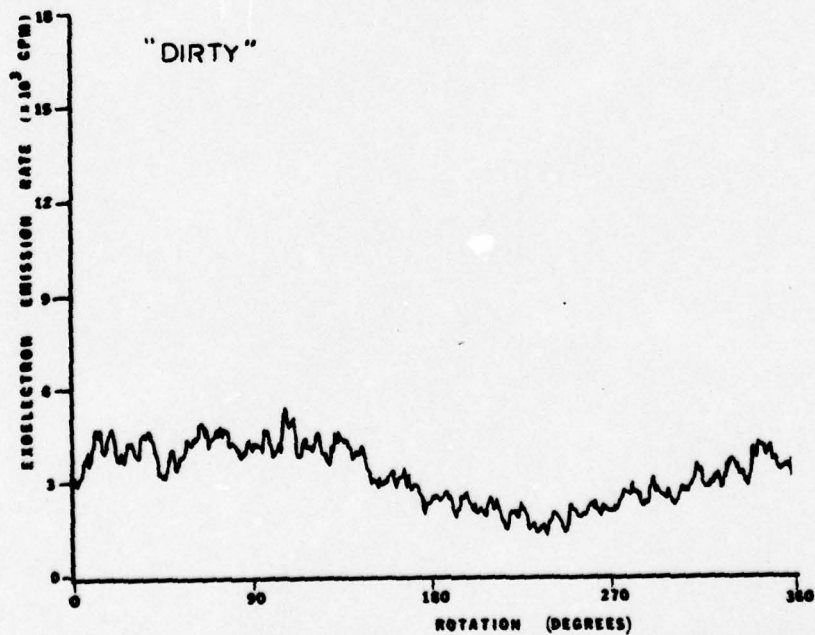


Figure 13 - EE from uncoated steel specimen after a wear test at 1000 grams with a 52100 steel pin; wear track not cleaned.



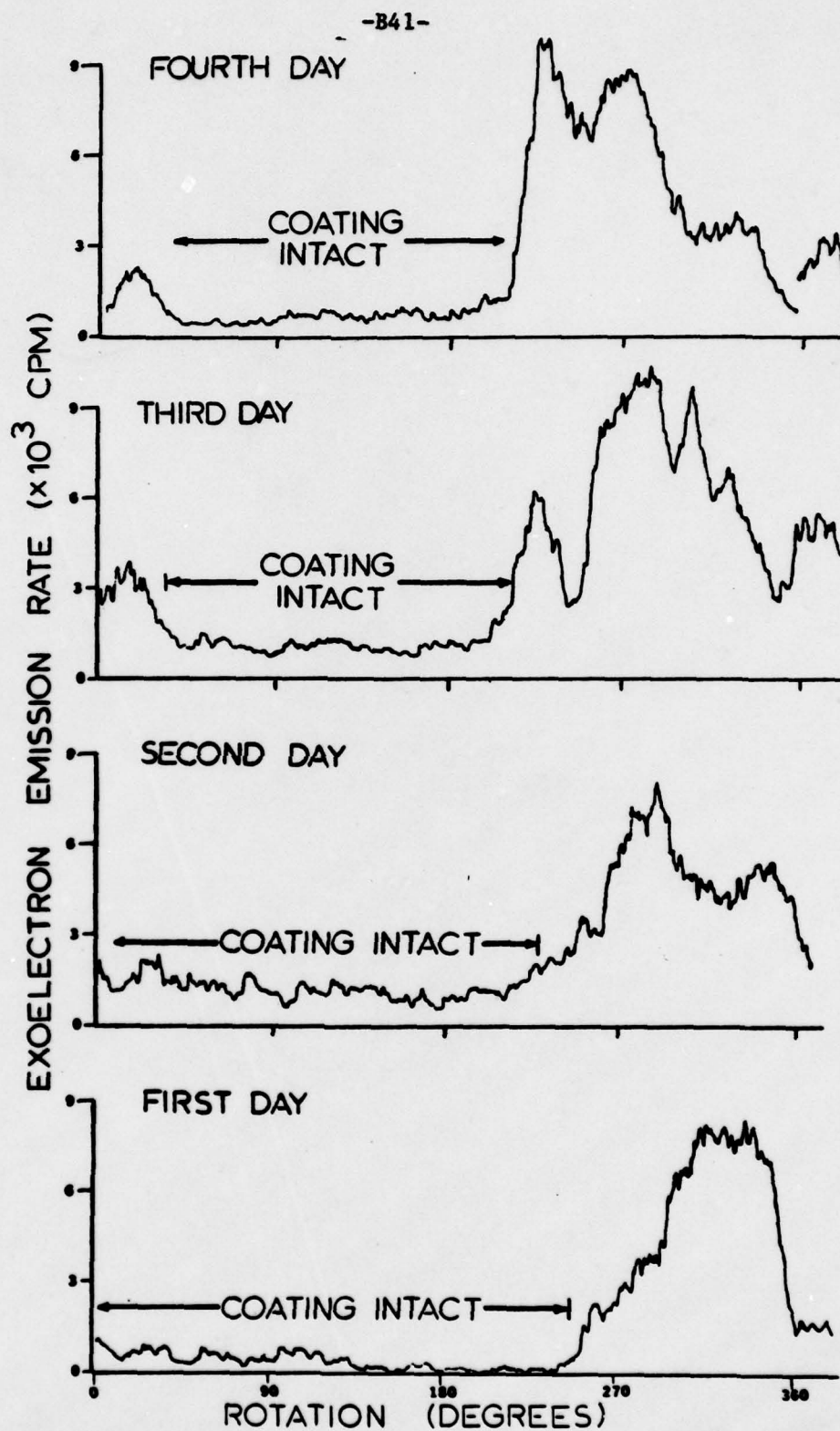


Figure 14 - EE from Rokide coated specimen over a four day period (50 hour wear test) at 500 gram load with a silicon carbide pin.

where the coating has worn away leaving an exposed metal substrate. One should note that the magnitude of the maximum EE peak is roughly the same (between 9000 and 10,000 cpm) even though the peak location is different, in each of the four plots. Also, note that the width of the so called "active area" increases from 90 to 180 degrees, reflecting the increasing area of exposed substrate.

In figure 15, the Rokide specimen produced an abrupt rise in exoelectrons, as seen just before the 180 degree line. This portion of the wear track was still coated, and therefore it was thought that our first premature defect had been sighted. Upon examination under the optical microscope, a small "S" shaped void was located in the same area that produced the EE rise. A photomicrograph of this defect is shown in figure 16. Unfortunately, further testing never produced a rise in emission from this spot again. Furthermore, this was the only time the exoelectron emission process and a pin-on-disk test produced a detectable defect in the coating.

After the EE scan shown in the last figure, the Rokide specimen was etched in 50% nitric acid. It was at this point that we realized a second coating, a nickel-chrome undercoat was present, as is common with flame sprayed oxides. This undercoating can be seen in figure 17. After acid etching, exoelectron plots were taken before and after a wear test. These are shown in figure 18. Note how much higher the EE count is where the Ni-Cr undercoat is exposed.

Friction measurements were taken as the coating wore away. The friction coefficient had a value of 0.18 for the silicon carbide pin

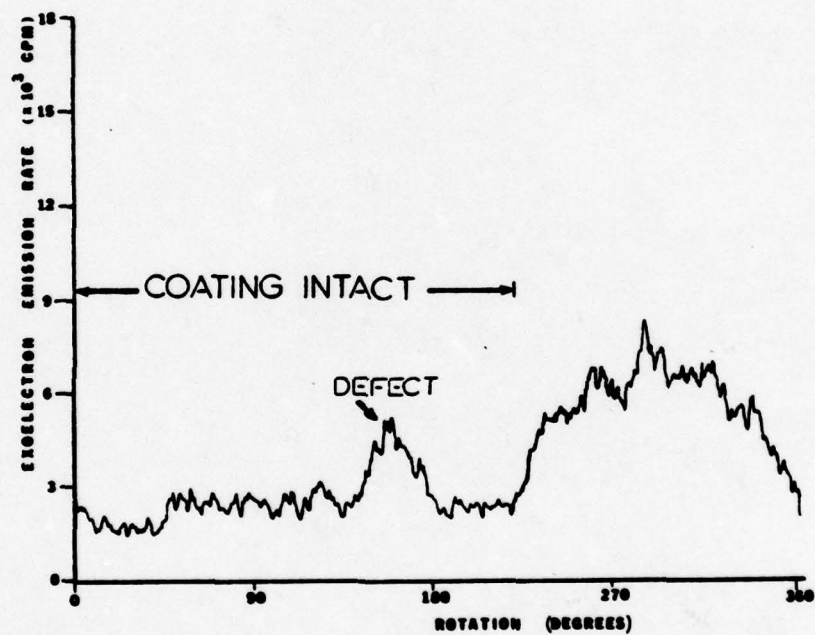
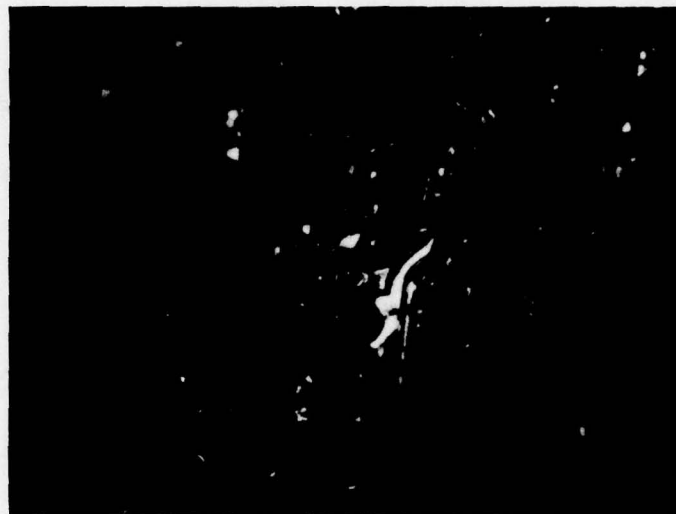


Figure 15 - EE from Rokide specimen with indications of a possible coating defect after a wear test at 500 grams with a silicon carbide pin.



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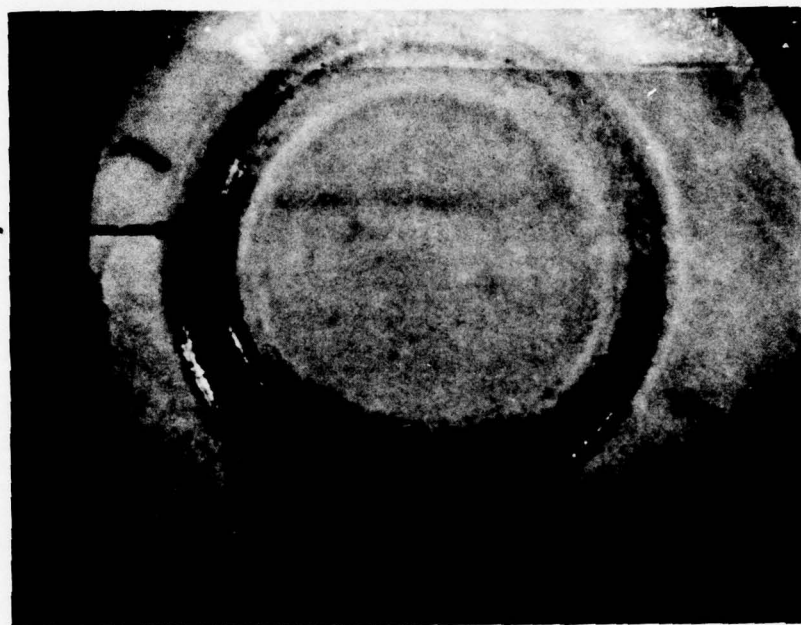


0 0.5 mm

Figure 16 - Photomicrograph of "S" shaped defect in Rokide coating corresponding to exoelectron peak in figure 15.

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NiCr  
undercoat



0 7.5 mm

Figure 17 - Photomicrograph of Rokide coated specimen showing wear track, steel substrate and nickel-chrome undercoat.

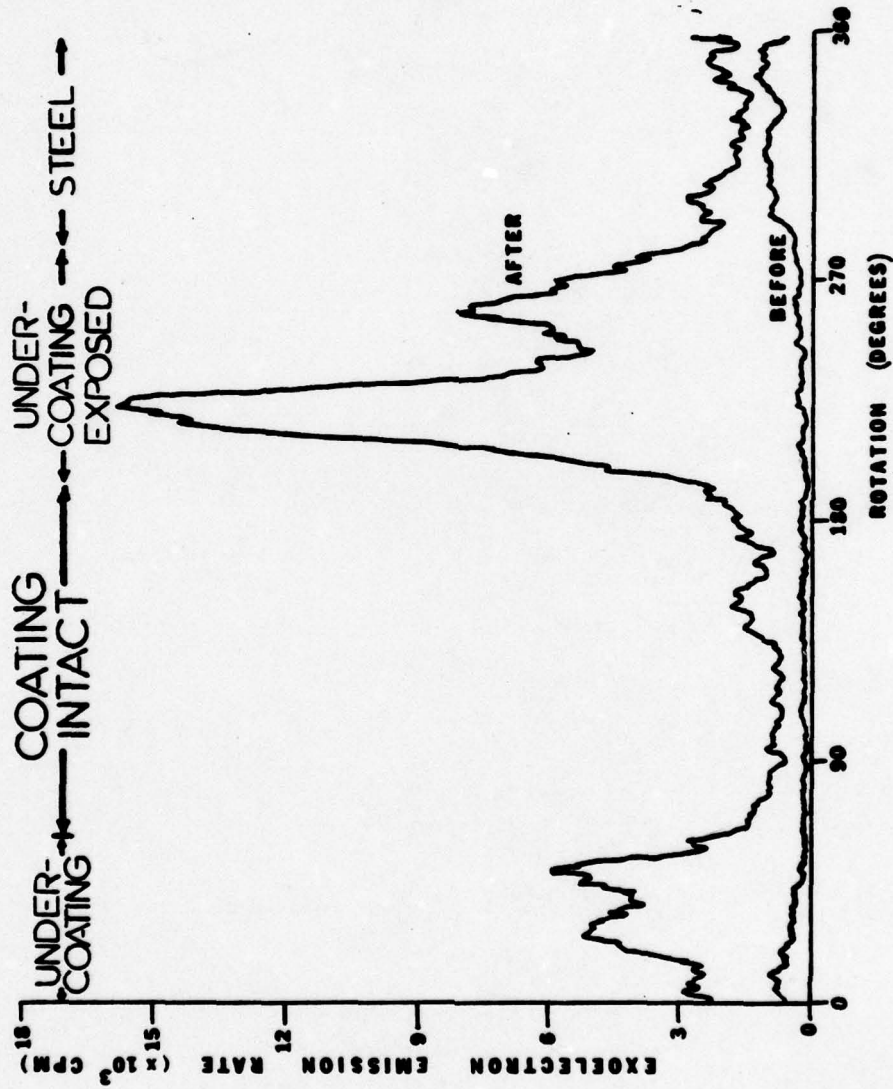


Figure 18 - EE from Rokide coated specimen after acid etching; before and after wear test at 500 grams with silicon carbide pin.



on the Rokide coating and a value of 0.35 for the same pin on the uncoated base metal. Figure 19 is a friction trace before the coating wore away while figure 20 is a trace after this had occurred. One can see the large jump in the friction force in the latter plot corresponding with that spot where there is no more coating.

After completing our tests with the Rokide, similar pin-on-disk tests were conducted with Union Carbide's coatings. A typical plot is given in figure 21 - in this case a coating of  $\text{Cr}_2\text{O}_3$  (deposited by the plasma-arc process) using a diamond impregnated pin at a one kilogram load and speed of 25 cm/sec. A portion of the  $\text{Cr}_2\text{O}_3$  was removed by us (figure 9) so that its thickness varied between one and eight mils.

An interesting phenomenon, not previously observed with the Rokide specimen, was noted. The coating itself (not the portion where the base metal was exposed) emitted a significant amount of exoelectrons during the initial test (figure 22). As the tests progressed, however, this "coating emission" decreased towards zero (e.g. figure 21).

Note also, that the diamond impregnated pin used in these tests, with a hardness many times more than that of the 52100 steel pin used in a steel on steel test, but at the same load, produced only a slightly higher rate of emission from the steel substrate (compare figures 12 and 21).

Unfortunately, we were unable to locate any defects in Union Carbide coatings using pin-on-disk wear tests. For reasons discussed

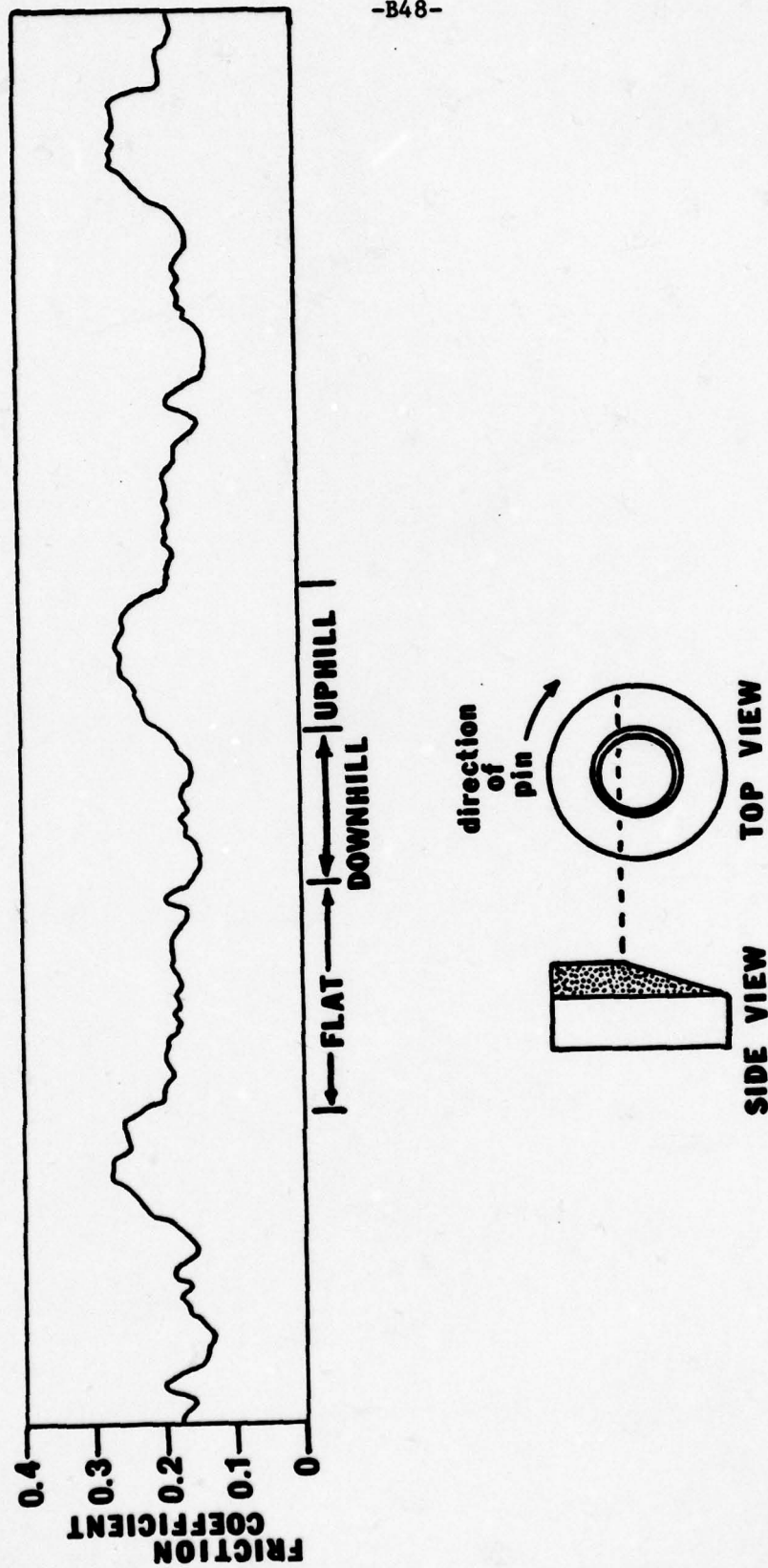


Figure 19 - Friction coefficient versus position for silicon carbide pin on Rokide coated specimen before base metal became exposed.

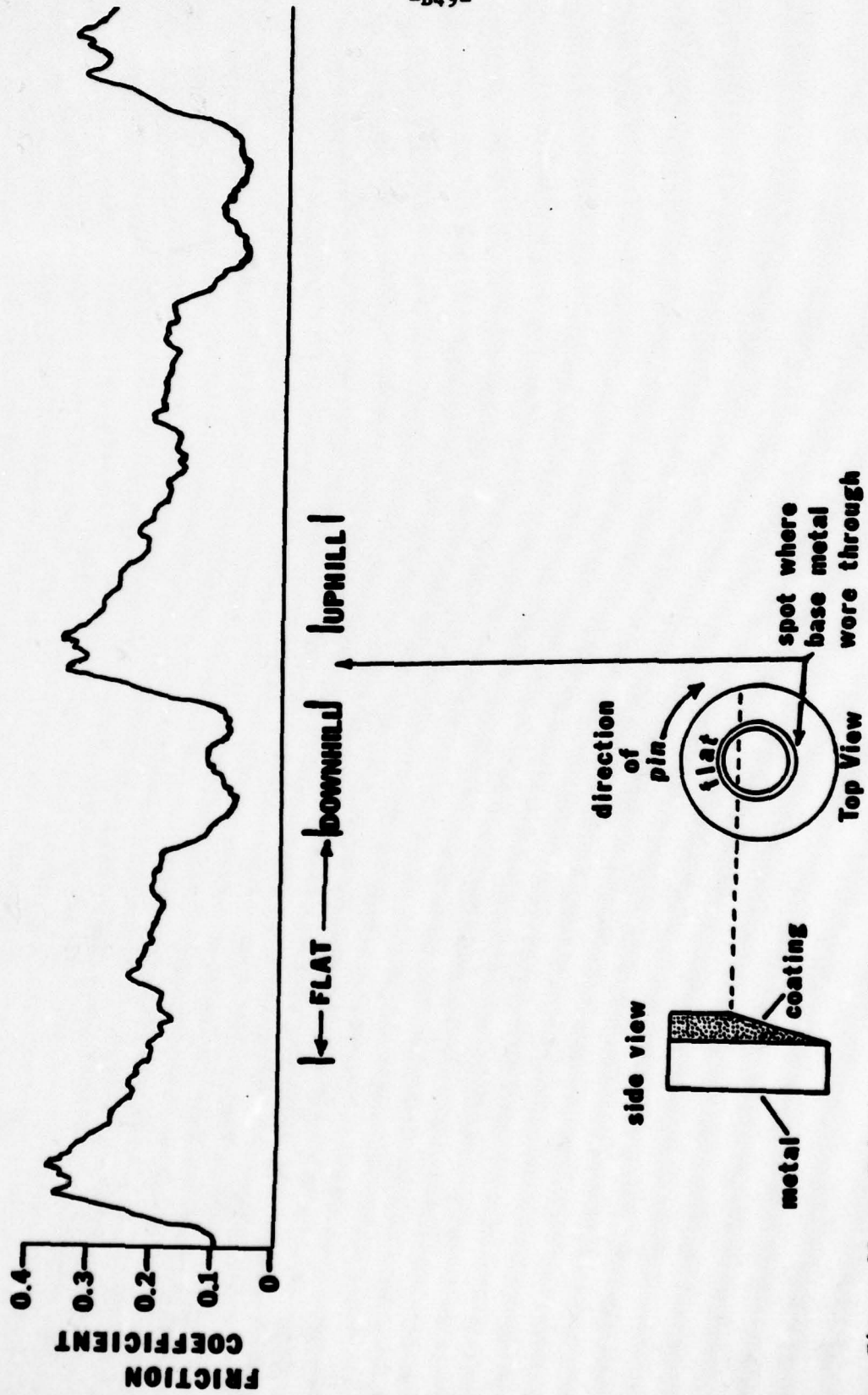


Figure 20 - Friction coefficient versus position for silicon carbide pin on Koxide coated specimen after base metal became exposed.



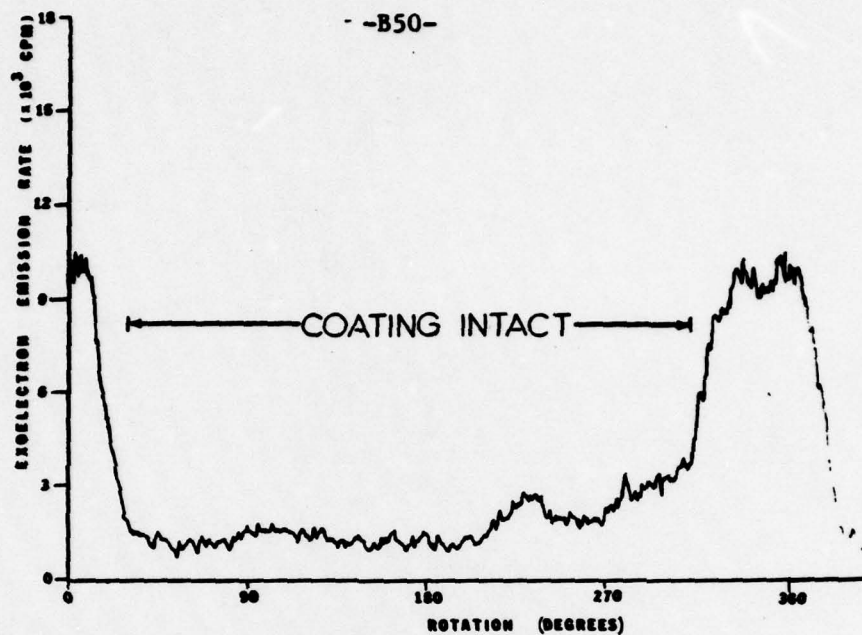


Figure 21 - EE from  $\text{Cr}_2\text{O}_3$  coated specimen after a wear test at 1000 grams with diamond impregnated pin.

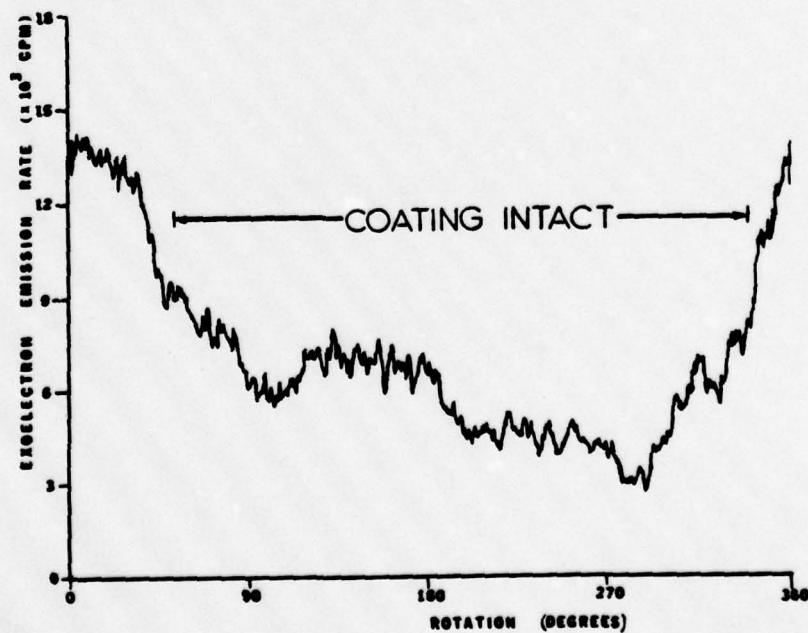


Figure 22 - Initial EE from  $\text{Cr}_2\text{O}_3$  coated specimen after first wear test, at 1000 grams with diamond impregnated pin.

later, we abandoned this method of trying to predict hard coating quality.

#### 4.3.2 Hard Coatings Subject to Surface Grinding

In the hope of producing defects, the alternative "semi-destructive" method of surface grinding was chosen. As noted before, no effort was made to grind 'properly'. Heat checking and pullout, therefore, were observed throughout the surface.

The emission of exoelectrons by the coating itself was, once again significant, as seen in figure 23 (a D-gun deposited  $\text{Al}_2\text{O}_3 + \text{TiO}_2$ ). The rate was similar to that obtained from the initial pin-on-disk tests, however, the emission did not drop after subsequent grinding runs.

After one grinding pass, the exoelectron emission showed two significant peaks as seen in figure 24. Examination by optical microscope revealed several pinholes where, apparently, the coating had been pulled from the surface. However, similar to the pin-on-disk defect, no EE peaks were observed after five additional grinding tests (a total removal of 2 1/2 mils). Figure 25 has a photomicrograph of the area which produced the two EE peaks.

#### 4.3.3 Solid Film Lubricants and Pin-on-Disk Tests

In our work with solid lubricants, we are concerned primarily with the process by which the coating is removed. Using a Teflon-HD coating which emits no exoelectrons, we were able to determine several things about the nature of Teflon wear in a pin-on-disk test.

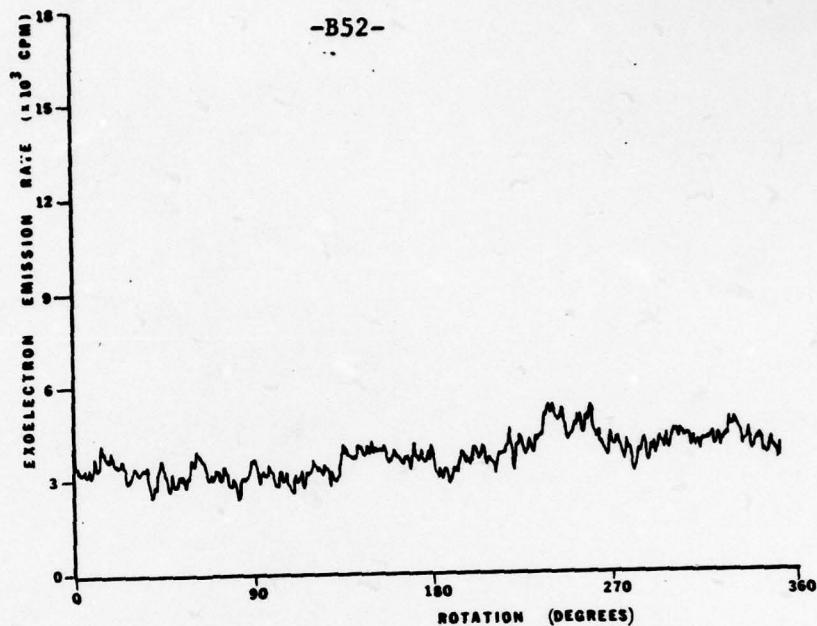


Figure 23 - EE from  $\text{Al}_2\text{O}_3 + \text{TiO}_2$  coated specimen after surface grinding with aluminum oxide wheel.

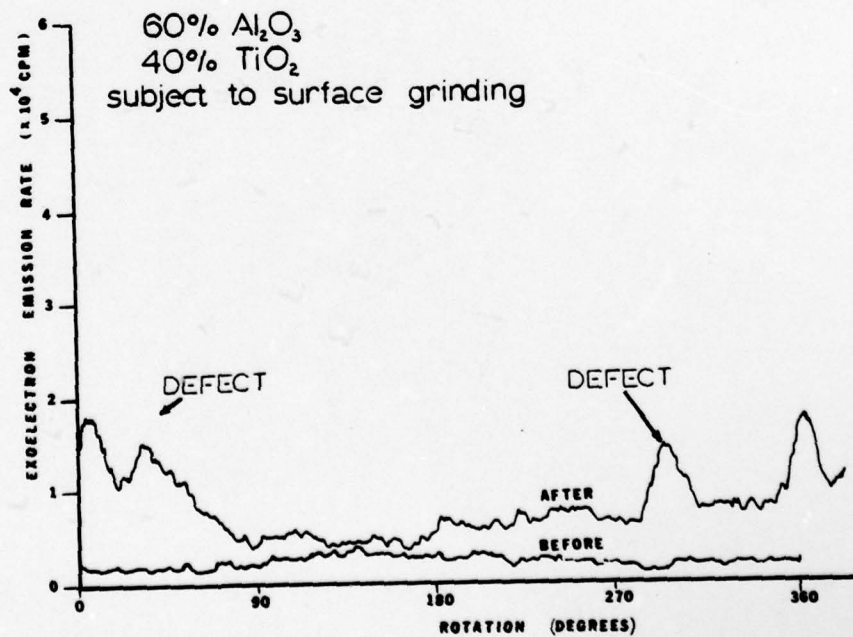


Figure 24 - EE from  $\text{Al}_2\text{O}_3 + \text{TiO}_2$  coated specimen before and after surface grinding with indications of possible defects in coating.



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**WHITE SPOTS ARE WHERE COATING  
HAS BEEN PULLED FROM SUBSTRATE**

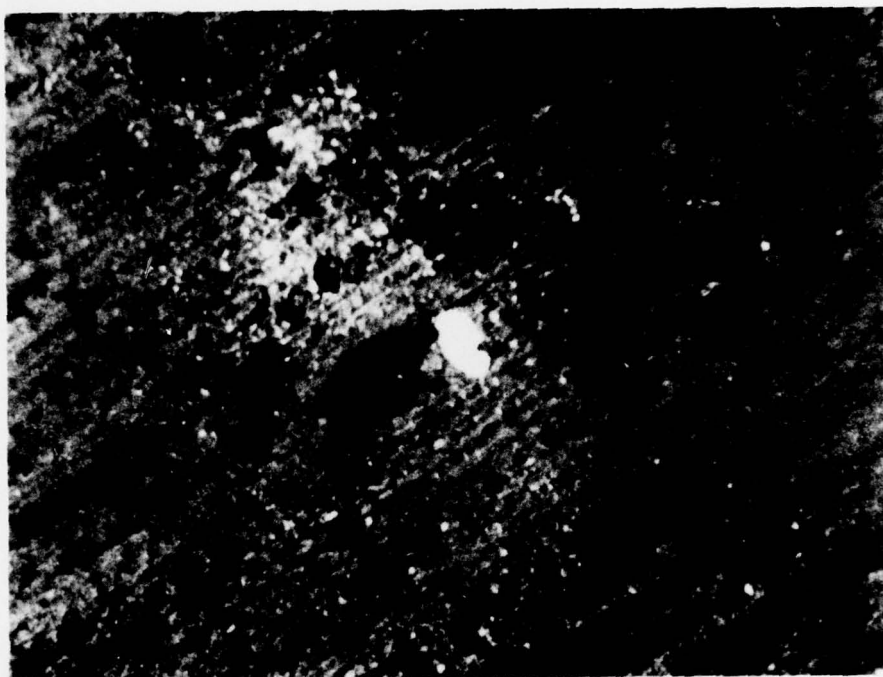


Figure 25 - Photomicrograph of  $\text{Al}_2\text{O}_3 + \text{TiO}_2$  coated specimen at the coated area which produced a rise in EE corresponding to figure 24.

The first thing determined was that some Teflon coating is transferred to the steel pin. This was verified through friction tests. After passing the pin over the Teflon coating, the same pin was transferred to a plain steel disk. At low speeds, the friction could be seen to increase from a value close to that for Teflon on steel, to that for steel on steel (but with stick slip). The actual friction trace is provided in figure 26.

Second, we noted that thin, transferred layers of Teflon can reduce a known EE count to almost zero. In this case a pure Teflon pin was run over portions of an active (i.e. freshly worn) steel surface. EE was noted before and after the Teflon was introduced. At the locations where the Teflon pin had contacted the surface, exoelectron emission dropped to zero, while on the remainder, normal decay had taken place, as seen in figure 27. Cleaning (with Freon degreaser) the same surface which had been "contaminated" with Teflon partially restored the EE count.

With the Teflon-HD sample, it took a relatively long time for both the friction and the EE rate to show any significant increase. When they finally did increase, it was in a simultaneous manner. The substrate on this particular sample had been prepared by belt sanding, leaving the steel with many tiny grooves. As the coating wore away, these grooves or ditches acted as tiny reservoirs of Teflon which the steel pin was able to pick up and transfer for small distances to the naked regions. Thus, even though parts of the wear track appeared devoid of any coating, both to the naked eye and under the microscope, exoelectron emission proved that small migrations of the film were

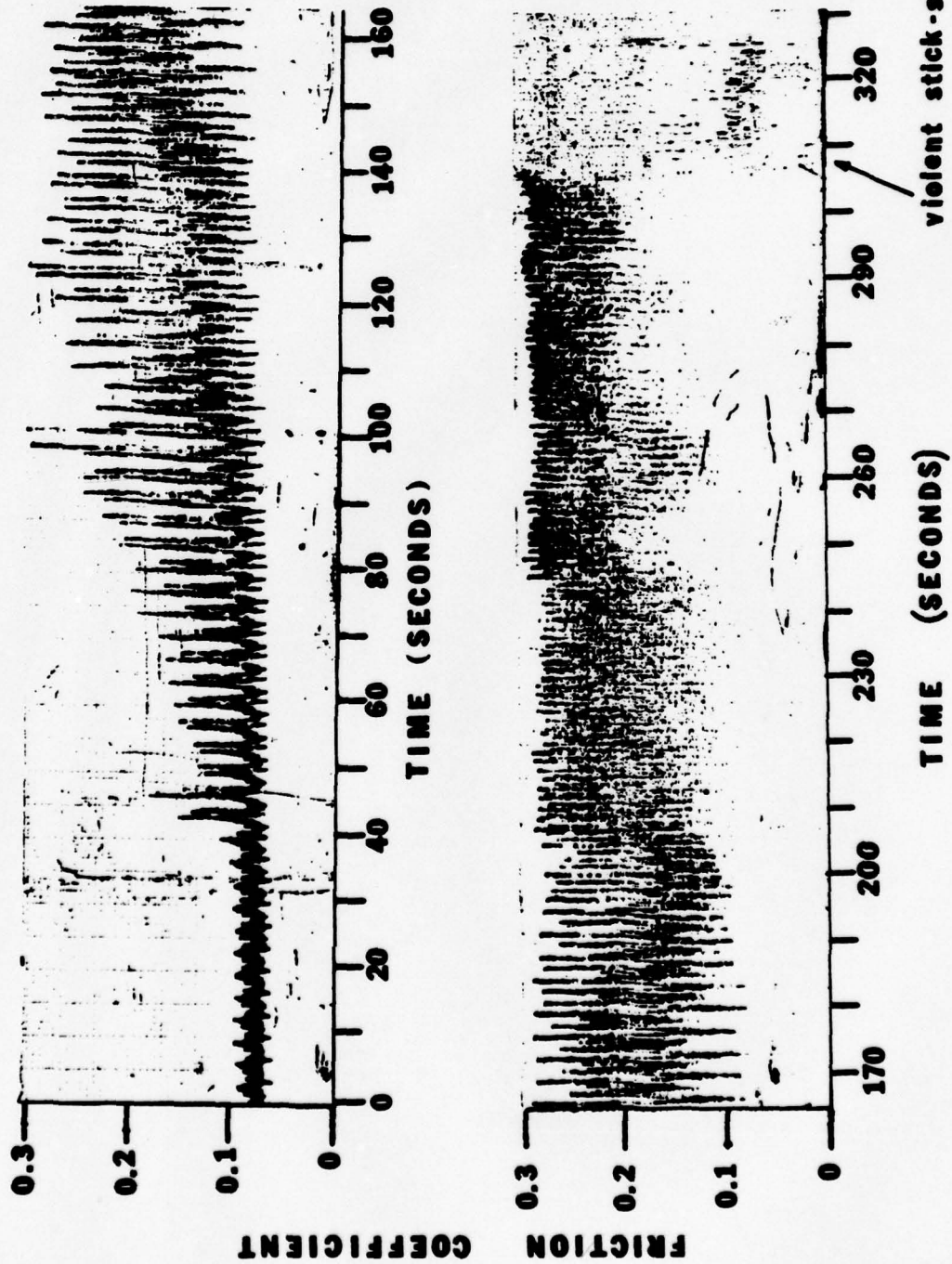


Figure 26 - Friction coefficient versus time from 52100 steel pin riding on plain steel, after steel pin had ridden on Teflon coating.



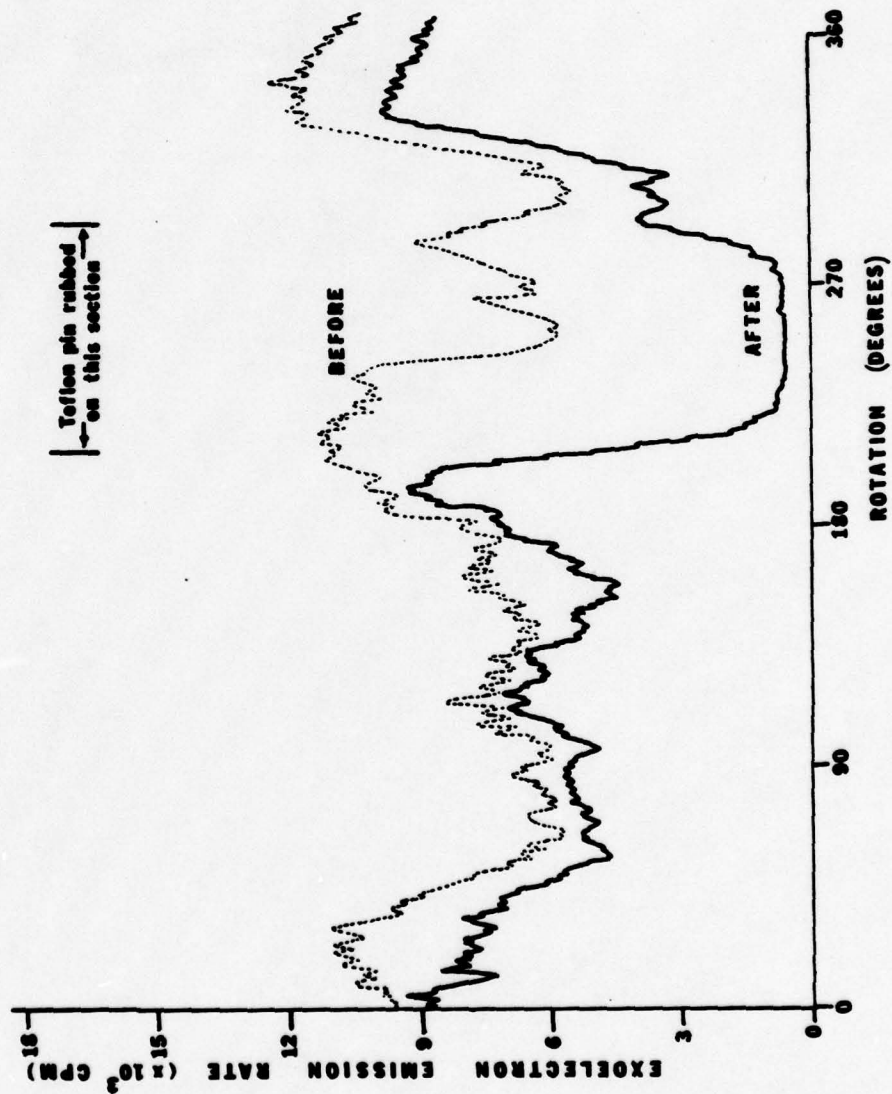


Figure 27 - EE from plain steel specimen; before and after rubbing a small portion of the fresh wear track with pure Teflon.

occurring. Figure 28 is a time history of EE versus position for the aforementioned sample. Figure 29 contains two photomicrographs of the track before and after the depletion of the "reservoirs." Likewise, figure 30 is a time history of the friction force versus position for the same sample.

#### 4.4 Discussion

The results of the tests conducted in air were mixed. It now appears unlikely that any semi-destructive test, together with exoelectron emission could be used to predict the life or quality of a hard coating. There are two important reasons for this. First, it is necessary to create or propagate a defect, and second, this defect must be detectable using exoelectron emission. Apparently, neither a pin-on-disk nor a surface grinding test is severe enough for promoting cracks through to the metal substrate. Naturally, most wear resistant coatings are extremely strong. For example, the tensile bond strength of the 87% WC + 13% Co coating exceeds 25,000 psi while, for compression, a bending stress of 140,000 psi is required to produce cracks in the same coating, which actually fails by shear. In most tests, the base metal will fail before the coating (25). In those rare cases when a crack does form, it may have one of several possible forms, as shown in figure 31. Of these forms, only one lends itself to being readily detectable using exoelectrons. The fact that fresh wear debris (both metallic and non-metallic) reduces the EE rate has already been noted and is probably due to the inability of the UV light to penetrate through to the larger area of the exposed base

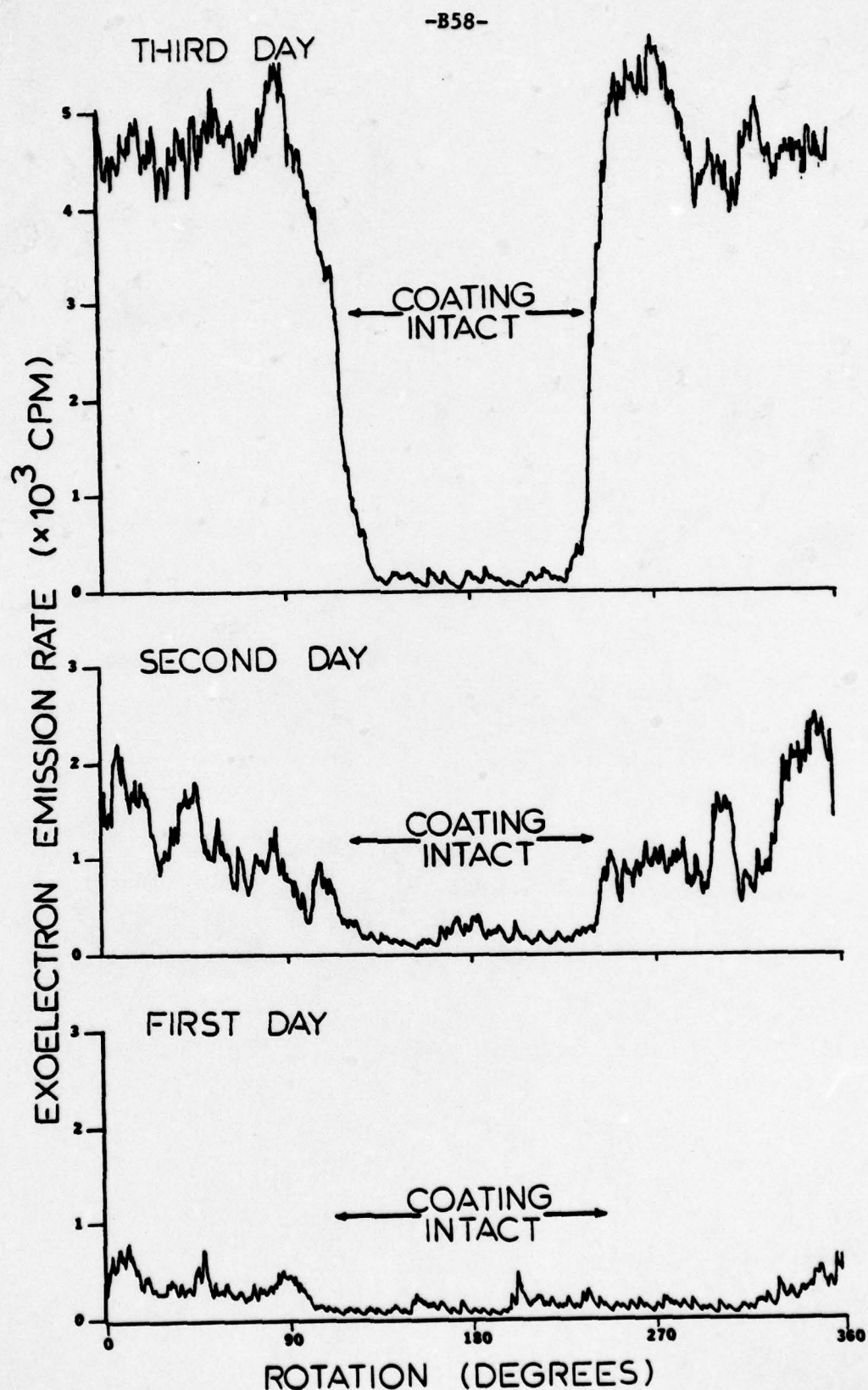


Figure 28 - Teflon-HD coated specimen (30 hour wear test) - 200 gram load  
- 52100 steel pin.



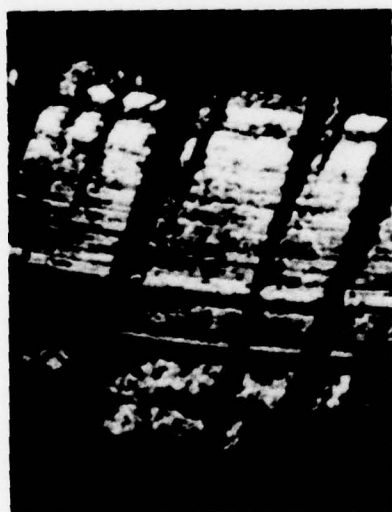
THIRD DAY



0 0.65mm



FIRST DAY



0 0.5mm

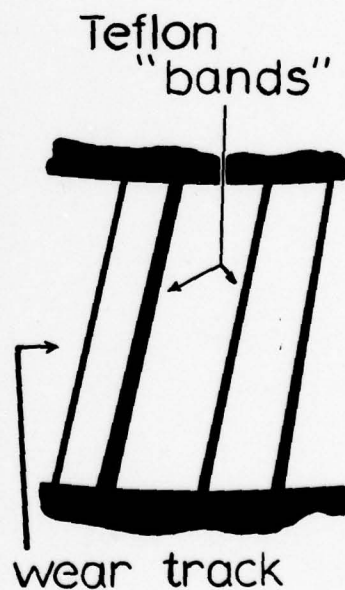


Figure 29 - Photomicrographs of Teflon-HD coated specimen's wear track corresponding to first and third day EE plots showing presence and then depletion of Teflon "bands."

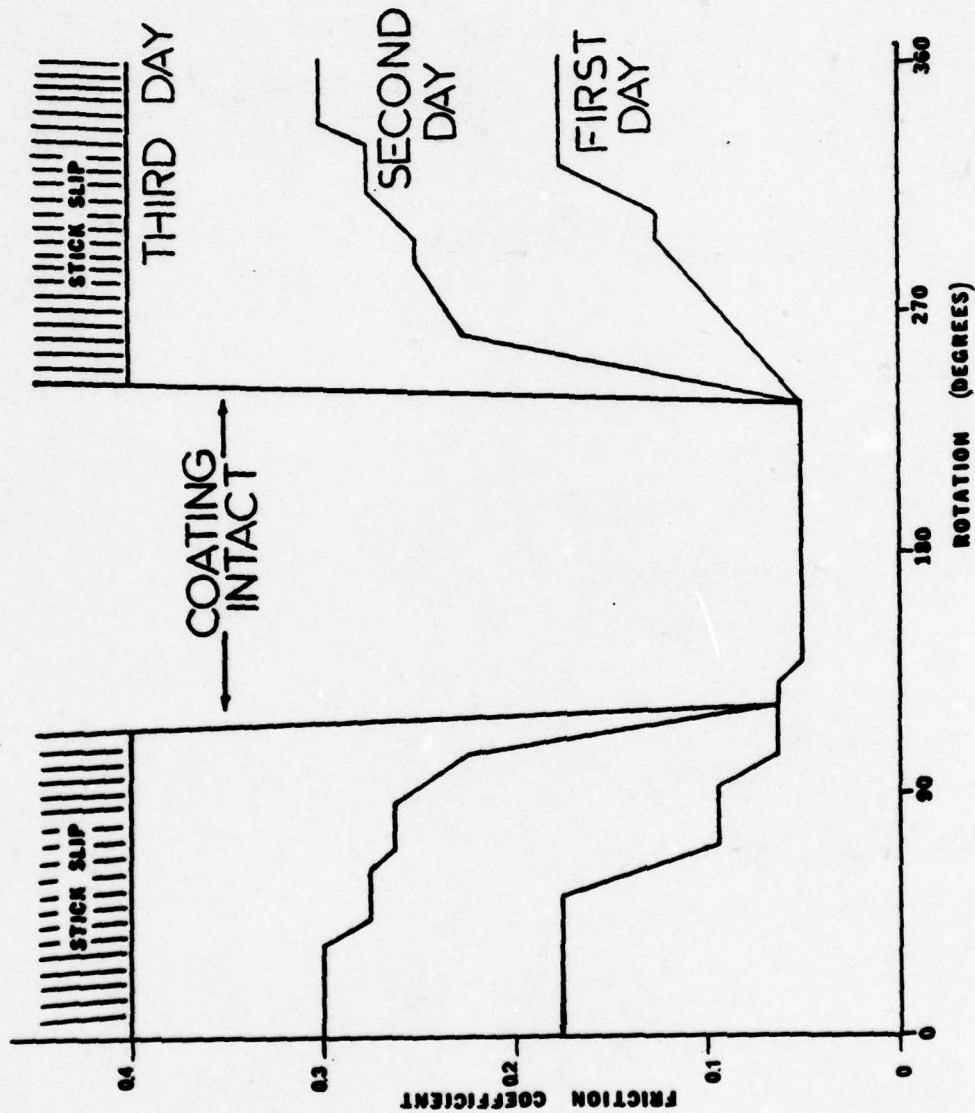
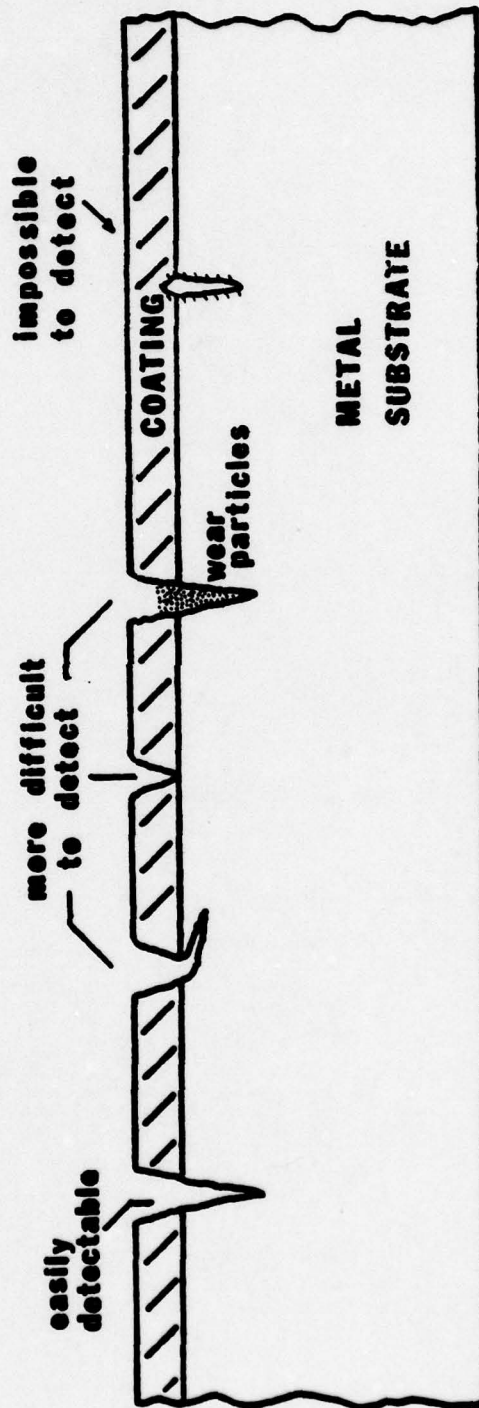


Figure 30 - Average friction coefficient over a three day period (30 hour wear test) with 52100 steel pin on Teflon-HD corresponding to figures 28 and 29.

DIRECTION  
OF →  
SCAN



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Figure 31 - Some possible coating defects and their detectability using exoelectrons.



metal. Obviously then, cleanliness is very important in obtaining the true EE history of the surface.

We also noted that the magnitude of the maximum EE peak does not change with the time history of a given wear test (e.g. figure 14). Unlike a growing crack which produces more and more surface area, the area deformed during wear is apparently constant and thus the maximum number of exoelectron emission sites per unit area remains constant. Why then, doesn't the count remain at a maximum throughout each scan of the bare base metal? First, the wear track might not have been thoroughly cleansed of wear particles. Second, the depth of the wear track may have dropped below the focal point of the UV light. Most likely, however, in the case of the Rokide coating, the nickel-chrome undercoat produced a much higher rate of EE when disturbed than did the steel substrate, leading to large variations in emission from the naked regions. Later tests, with specimens without undercoatings, showed very little variation in emission from exposed areas (figure 32). Figure 18 would seem to prove that, indeed, the undercoating is responsible for the varying emission from the Rokide specimen.

The idea that rate and behavior of exoelectron emission might be related to the type of wear involved was abandoned. Since wear tests on steel substrates used pins ranging from diamond to steel, the type of wear ranged from abrasive to adhesive. The rate of EE was independent of the pin employed but was dependent on the applied load. For example, a similar exoelectron emission rate was obtained from both steel on steel and diamond on steel tests using equivalent loads and

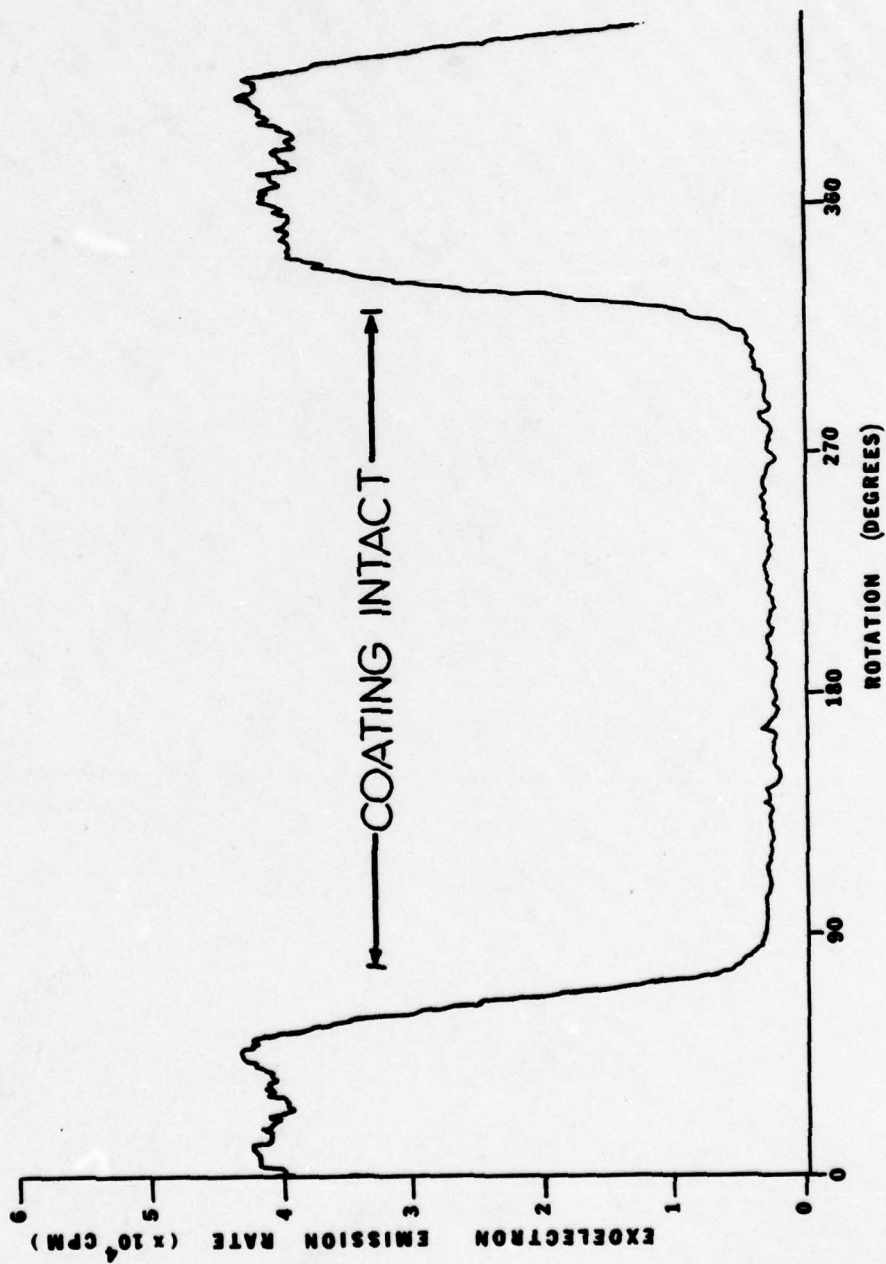


Figure 32 - EE from  $\text{Cr}_2\text{O}_3$  coated specimen after a wear test at 2500 grams with a diamond impregnated pin.

pins of the same diameter (figures 12 and 21). However, when the load was increased from 1.0 kg to 2.5 kgs with diamond on  $\text{Cr}_2\text{O}_3$  coated specimen, the EE rate increased from 10,000 to almost 40,000 cpm (figures 21 and 32). The rate of decay of exoelectron emission in air and vacuum also did not depend on the type of wear involved. It seems, therefore, that exoelectrons are best suited for measuring the relative severity of wear. However, we cannot say, for example, that an EE rate of between 1000 and 20,000 cpm is achieved under adhesive conditions only and that rates above 20,000 cpm are only observed under abrasive conditions. Exoelectrons, a surface area phenomenon, are unable to differentiate by themselves between the different wear processes, a volumetric phenomenon.

Of course, in all cases, exoelectrons were found to be an excellent tool for locating those spots where the film (both hard and soft) had worn away. EE still has some advantages over the conventional friction testing method, even though both were found to increase simultaneously. Some of these advantages include the potential ability to monitor much larger areas and the fact that it is unnecessary to conduct measurements during a wear test (29).

The fact that some of the wear resistant coatings emit a significant amount of exoelectrons when disturbed might, at first, loom as a major obstacle. Why these non-metallic oxides and carbides undergo EE at all, is left unanswered but the fact that fresh surfaces of steel and aluminum produce a higher rate than these coatings reduces the "obstacle" to a mere nuisance. We were still able to locate defects



from the  $\text{Al}_2\text{O}_3 + \text{TiO}_2$  coated specimen (subjected to surface grinding) and also locate those spots where the coating had worn away from the  $\text{Cr}_2\text{O}_3$  coated specimen (pin-on-disk) even though both coatings emitted a substantial number of exoelectrons. The reason coating emission decreased with subsequent pin-on-disk tests but remained fairly constant after each grinding run might be attributed to the constant "reorientation" of the surface in the latter case ("re-orientation" would only occur in the initial pin-on-disk test). Of course these questions might be better answered when an acceptable theory for the exoelectron emission mechanism is reached.

Finally, we were able to conclude that exoelectrons are an ideal way for studying the migration of films along the wear track. The fact that exoelectrons are easily stopped makes detection of even the thinnest transfer films possible. This is especially advantageous if the film is invisible, as Teflon tends to be. It was found that the distances travelled by these films is very small (no more than a few millimeters). For example, after the last scan shown in figure 28, when one half of the wear track was Teflon coated and the other half was bare, no "long-range" migration was observed from the coated to the naked region. Transport of films was only observed with the presence of the so-called "ditches" (i.e. when the widths of the bare regions was minimal).

## CHAPTER 5

### EXOELECTRON EMISSION AND SPECIMENS TESTED IN VACUUM

#### 5.1 Introduction

Heretofore, all the experiments that were carried out were done so "discontinuously" - that is, the wear or grinding test was halted, the specimen moved to the vacuum chamber and then, the wear track was scanned for EE. But this procedure really only reflects what occurred several minutes ago, on the very last pass the rider made over the surface. Unless we are willing to go through the tedious procedure of transferring the test piece after almost every revolution, our ability to observe short term trends is greatly reduced. Furthermore, at atmospheric pressure EE decays rapidly and by the time the surface is scanned, we may have already reached emission half-life.

Wear, of course, is a dynamic phenomenon. Therefore, if one is to study it using exoelectrons, perhaps a better way to do so is while the wear is actually occurring. It was decided that the construction of additional apparatus was warranted so that simultaneous wear, friction and EE tests could be conducted in the evacuated chamber, as described in section 3.2.

Only two reports could be found in the literature which discussed the results of previous simultaneous exoelectron and wear tests. Both reports were found in Soviet publications and both accounts only dealt with experiments conducted in air at atmospheric pressure (11, 23). The discussions and results were of a general nature, giving exoelectron emission rates as a function of time, not position along

the wear track. The initial wear period was always characterized by the most rapid growth in the EE rates which would then either gradually level off or continue to grow but at a much slower pace (at loads up to 15 kg). If the load was removed, but the specimen continued to rotate, a slow decrease in EE with time was noted. The two papers both sought to ascertain if exoelectrons could reflect the changing nature of surface layers (not coatings) during the wear process and both concluded that the simultaneous tests "afford promising possibilities."

In contrast, our tests were more specific in nature. Their purpose was to study the wear and possible migration of solid film lubricants in vacuum using exoelectrons.

Before proceeding, it should be recalled that there is a marked difference in the behavior of exoelectron emission between a fresh surface created in vacuum and a fresh surface formed in air at atmospheric pressures. As far back as 1953 it was noted that EE was connected with, among other things, the interaction between gas molecules (presumably oxygen) and the virgin surface (13). Some researchers stated that the chemical reaction between the naked metal and oxygen provided the necessary energy for EE. Later, others argued that the adsorption of water vapor has a decisive effect in lowering the work function, resulting in the initial growth of PSFE which then decays with the growth of an oxide film (30).

The pressure (more specifically the partial pressures of either water vapor and/or oxygen) plays a dominant role in emission from abraded specimens. EE has been found to be negligible at total pres-



tures below  $10^{-8}$  torr. In addition, as the pressure increases (from  $10^{-8}$  torr), the magnitude of EE increases and the time interval for reaching maximum emission decreases. In 1975, Baxter brought to light the fact that, contrary to the aforementioned behavior of scratched specimens, emission from specimens plastically deformed in vacuum exhibited no time dependence (1).

The lowest pressure we could achieve with our vacuum system was  $10^{-5}$  torr. At this pressure, the time interval to reach maximum emission is reported to be only about 10 seconds (13, 30). In our case, this works to our advantage because of the 15 second delay encountered from the time the pin traverses a certain spot, till the UV light strikes that same location. The rate of decay at  $10^{-5}$  torr is, of course, very slow. Therefore, the only major difference between our wear tests in vacuum and those at atmosphere, would appear to be that, now, the magnitude of EE will be much less. However, even this may be deceiving, because there was usually more than a 10 minute delay between the atmospheric wear test and the EE scan, by which time the rate of emission had declined significantly.

As we said, the major aspect of these tests dealt with the possible migration of solid film lubricants. If an "active" wear track were to have an organic material somehow transfer onto it, a significant drop in EE would be noted, as was shown in section 4.3.3. Now, however, we are in a position which enables us to "watch" any possible film movement as it occurs.

## 5.2 Procedures

For these tests, aluminum was chosen as the base metal because it tends to give off more exoelectrons than steel. Standard stock bars of 6061 aluminum were machined to the necessary dimensions. All of the solid lubricants that were then applied were rubbed onto the surface by us. The molybdenum disulfide was produced by Dow Corning in powder form and met the requirements of MIL-M-7866. The Teflon was of pure solid bar form as was the graphite. The aluminum disk was abraded with 1/0 emery paper before applying any of these lubricants. Also, after abrading and coating the surface, we usually waited at least 24 hours before starting a simultaneous test so that emission from the aluminum would not be "artificially" high. Finally, the pin used in all the experiments was 52100 steel.

To commence a test, the coated aluminum is placed inside the positioning fixture which is then placed inside the vacuum chamber. Before evacuating the chamber, the system is reset to zero, and the normal load applied via the extension spring arrangement shown in figure 6. The magnitude of this load can be determined from either the strain gage/preamplifier arrangement or by measuring the elongation of the spring knowing the spring constant (due to unequal distances from the pivot, the force exerted by the pin is only one-fourth the spring force). The normal load and vacuum are maintained by tightening the Swagelok connector. Before closing the chamber, the friction is zeroed, the UV light focused and the bias voltage applied. Finally, the system is pumped down to  $10^{-5}$  torr. The high voltage is then applied across the CEM (note that a background scan can no longer be taken because the load cannot be removed while maintaining a vacuum). The

AC motor is switched on to start the wear test which is conducted at a speed of 1 cm/min (1 rpm). After one complete revolution, the wear test would usually be momentarily stopped so that the X-Y recorder could be reset to zero.

### 5.3 Results

Our first tests were run with an uncoated aluminum disk. We were interested in seeing just how different our results would be from wear tests conducted in air. With no load applied, an initial background scan was taken. Then a load of 500 grams was applied to the pin and the wear test was begun. EE was noted during each revolution and recorded whenever there was a notable change. After thirty revolutions the test was stopped. Laboratory air was then admitted to the vacuum chamber which reverted back to atmospheric pressure for approximately one minute during which time the load was removed from the pin. The chamber was then once again evacuated and an exoelectron scan of the "old" wear track taken. The resulting plot is shown in figure 33. It can be seen that emission increased (slowly) over the entire track after each revolution. The largest jump in emission was noted upon the very first pass with the difference between subsequent revolutions gradually diminishing. Perhaps the most significant result relates to the exoelectron emission after air was introduced into the chamber (represented by the dashed lines in figure 33). EE was only slightly higher (if at all) than the thirtieth pass until the center portion of the scan was reached. There, a dramatic, almost twofold increase occurs for some time before the emission slowly goes



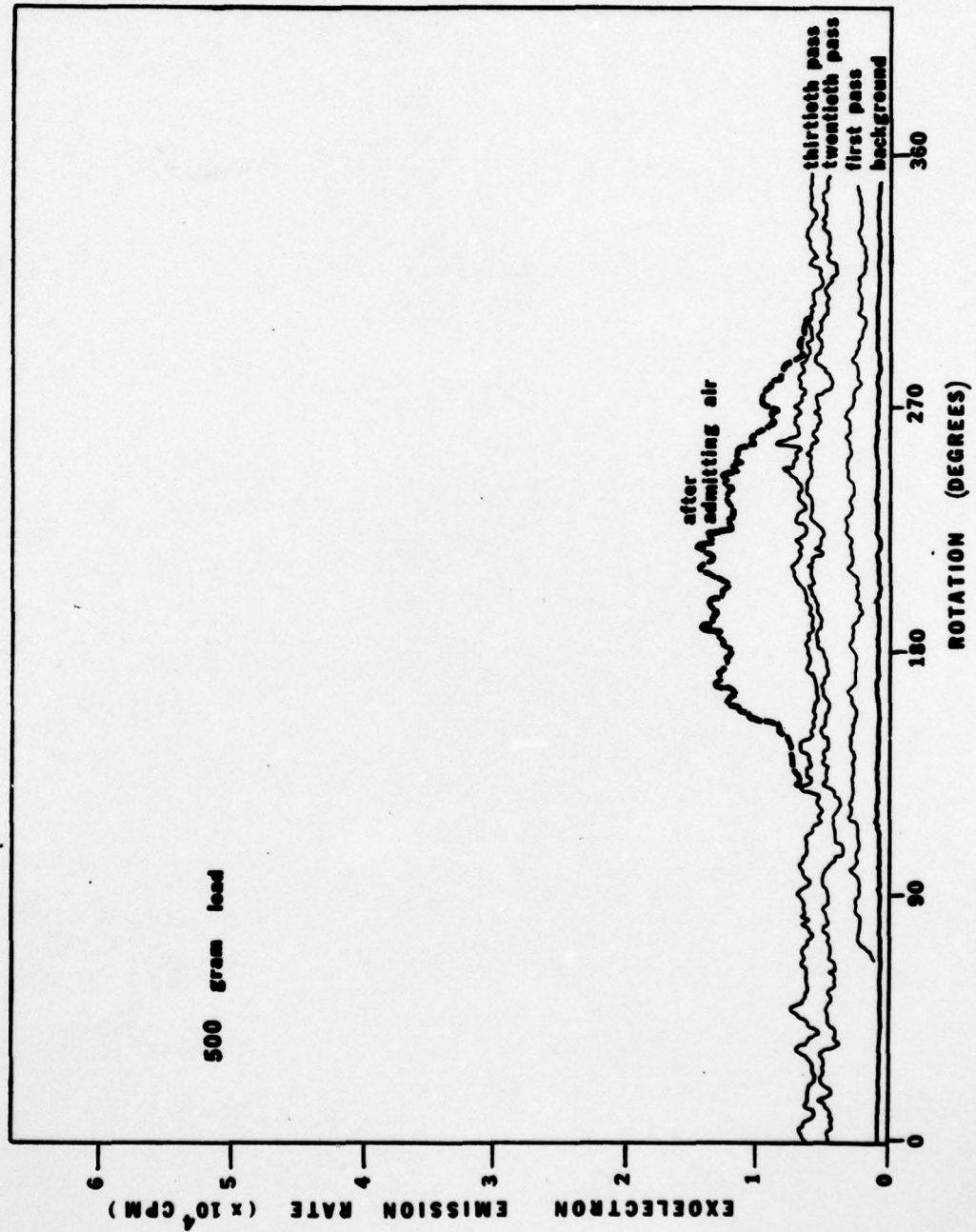


Figure 33 - EE from uncoated aluminum during simultaneous wear test at 500 grams and then at no load after admitting air to chamber.

back, once again, to the value obtained for the thirtieth revolution.

We then moved on to study aluminum coated with various solid lubricants. The first of these was molybdenum disulfide. We wanted to see how long the coating would take to wear out if it was merely rubbed on and to see how the emission behaved in the presence of a lubricant. The  $\text{MoS}_2$  covered the entire surface and a load of 500 grams was used. The results are given in figure 34. Apparently the load was too high because emission was noted on the very first pass. The results thereafter were similar to those obtained with the plain aluminum sample except for the fact that after about the twentieth revolution, the emission reached a maximum, where it remained for the remainder of the wear test.

It was decided to go to a lighter load so as not to break through the film so quickly. Also, in order to be in a better position to look at migration, it was decided to cover only half the specimen with lubricant and to leave the other half bare. The results of one of these tests, conducted at 100 grams with friction force measurements taken simultaneously, are shown in figures 35 and 36. The  $\text{MoS}_2$  in this case, did not completely breakdown until the twentieth revolution, which is reflected in both the EE scan and the friction trace. (Note that in the exoelectron figures, whenever part of a run produced the same rate of emission as the test sketched before, only the previous scan is shown, e.g. in figure 35, a part of both the second and sixth EE trace is unchanged from the background run). No evidence of lubricant migration could be found from either the friction force or exoelectron emission measurements. In fact, the film seems to lose its

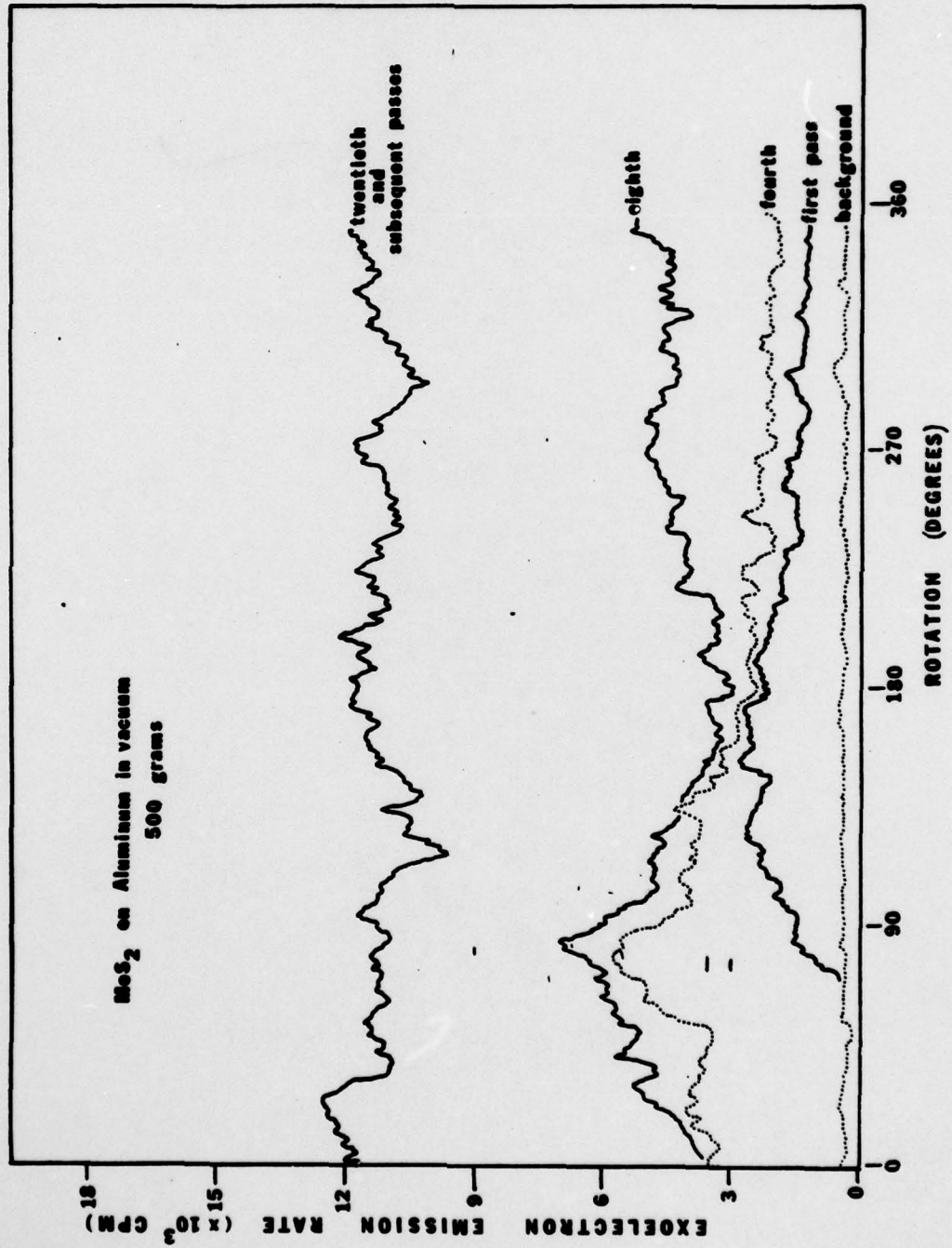


Figure 34 - EE from MoS<sub>2</sub> coated aluminum during simultaneous wear test at 500 grams with 52100 steel pin.



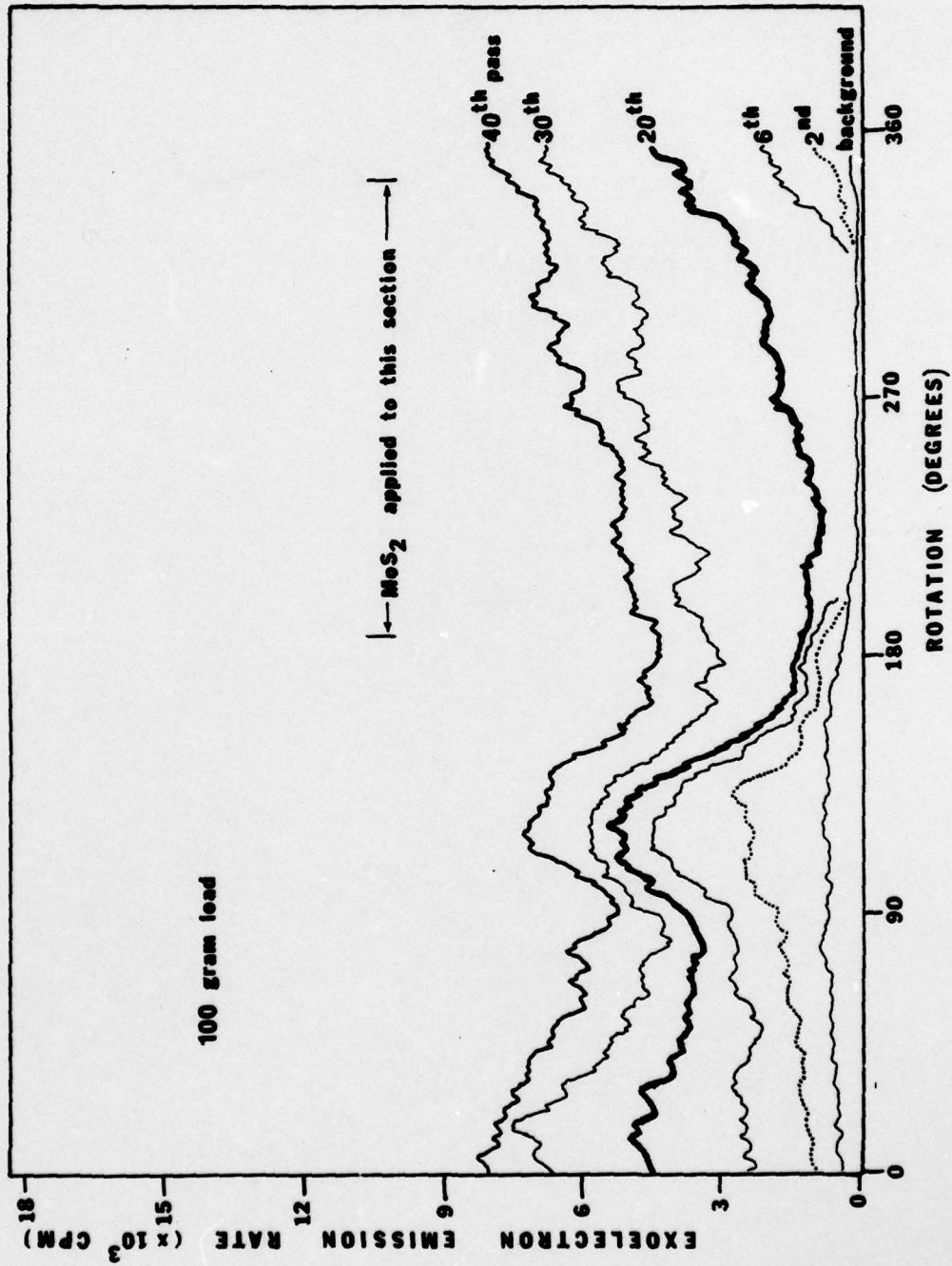


Figure 35 - EE from Partially MoS<sub>2</sub> coated aluminum during simultaneous wear test at 100 grams with a 52100 steel pin.

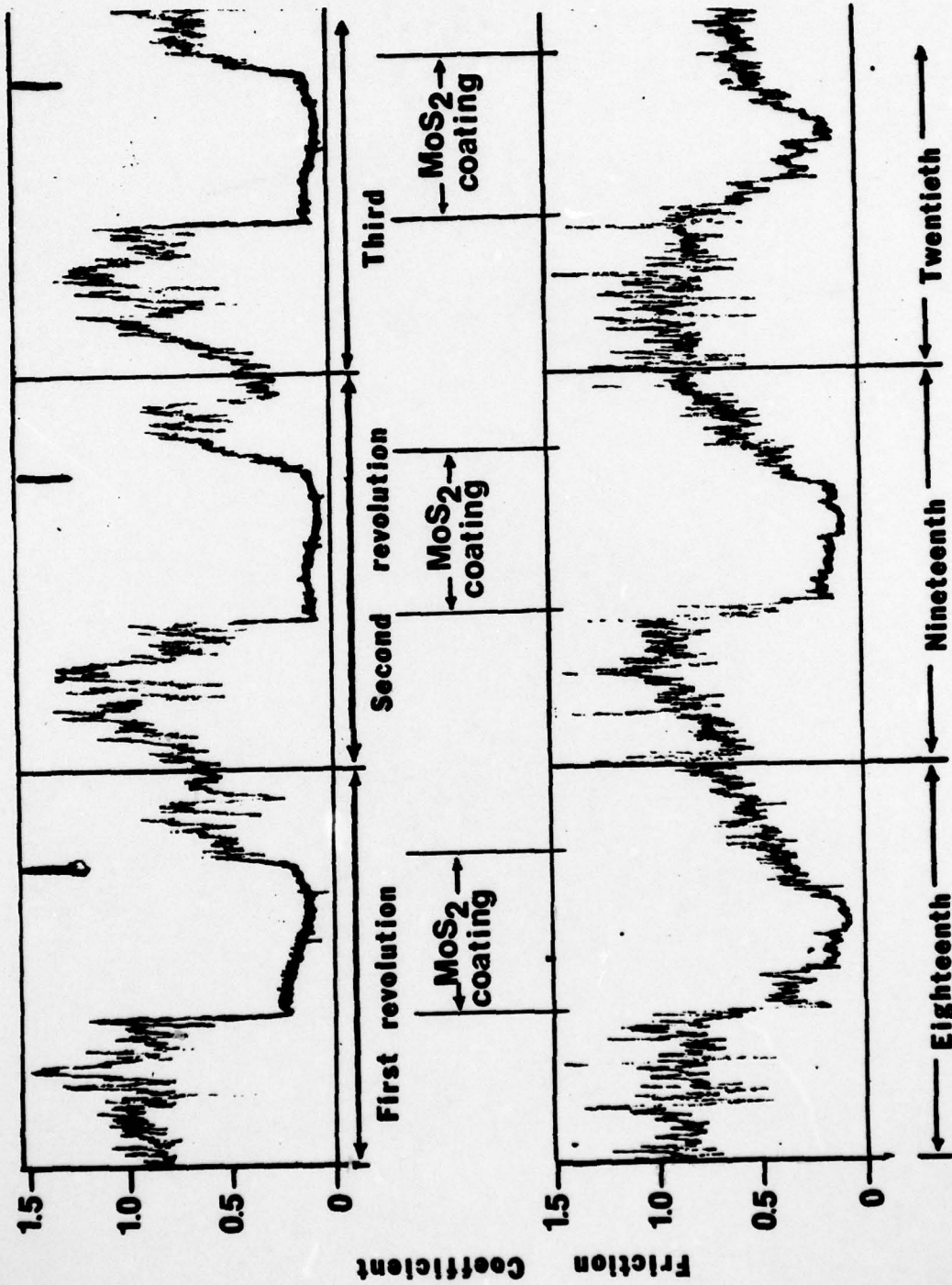


Figure 36 - Friction coefficient versus position for partially MoS<sub>2</sub> coated aluminum during test shown in figure 35 on six different passes (leads EE trace by approximately 90°).

integrity on the far side of the coated section first and in the end, finally breaks down in the center. This can be seen as the low point in the twentieth friction trace and the corresponding low point in the twentieth EE scan (just to the left of center of the coated section). After complete film rupture, the exoelectron emission behaved characteristically as before, increasing slowly but steadily to an apparent maximum on the fortieth pass.

Our next tests were with graphite as the solid lubricant. From a stick form, it was similarly rubbed on to one-half the aluminum (semi-circular area) and once again a 100 gram load was used. Results of a typical test are shown in figures 37 and 38. Again, the coating first wears from the far side of the coated area finally losing complete coherence on about the thirtieth revolution. No evidence of migration, using either the friction or EE trace, was evident.

The final solid lubricant tested was Teflon applied to half the aluminum specimen (semi-circular area) and again a 100 gram load was employed. Results are given in figures 39 and 40. The coating wore away rapidly and by the twelfth revolution both friction and EE scans indicated that no more Teflon was present on the wear track. The test was continued, however, and during the fourteenth revolution a huge drop in the friction coefficient was noted. Likewise, on the fifteenth EE scan, a notable decrease in emission was observed over almost the entire track. Subsequent revolutions produced a gradual rise in both friction and EE to their former levels.



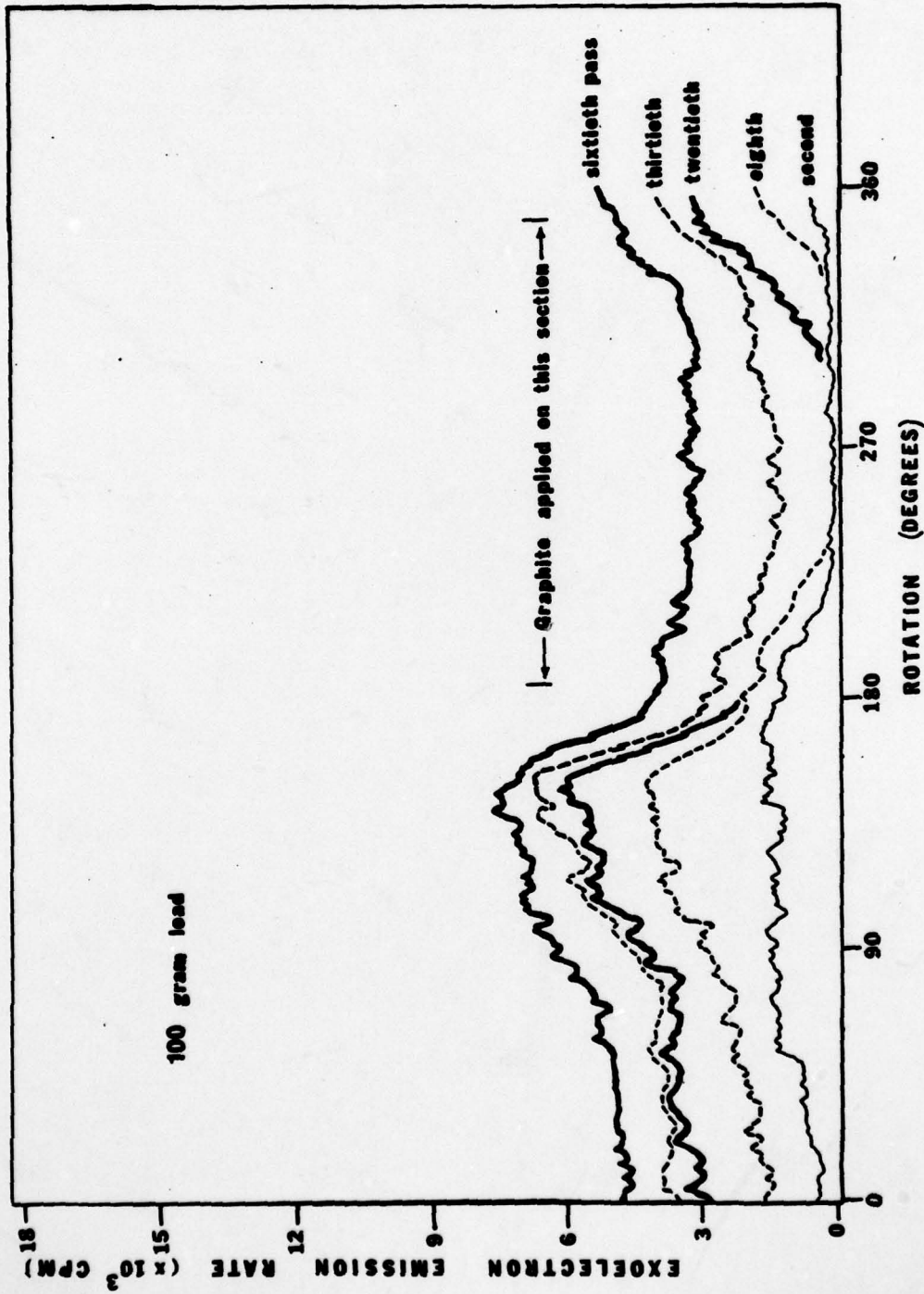


Figure 37 - EE from partially graphite coated aluminum during simultaneous wear test at 100 grams with 52100 steel pin.

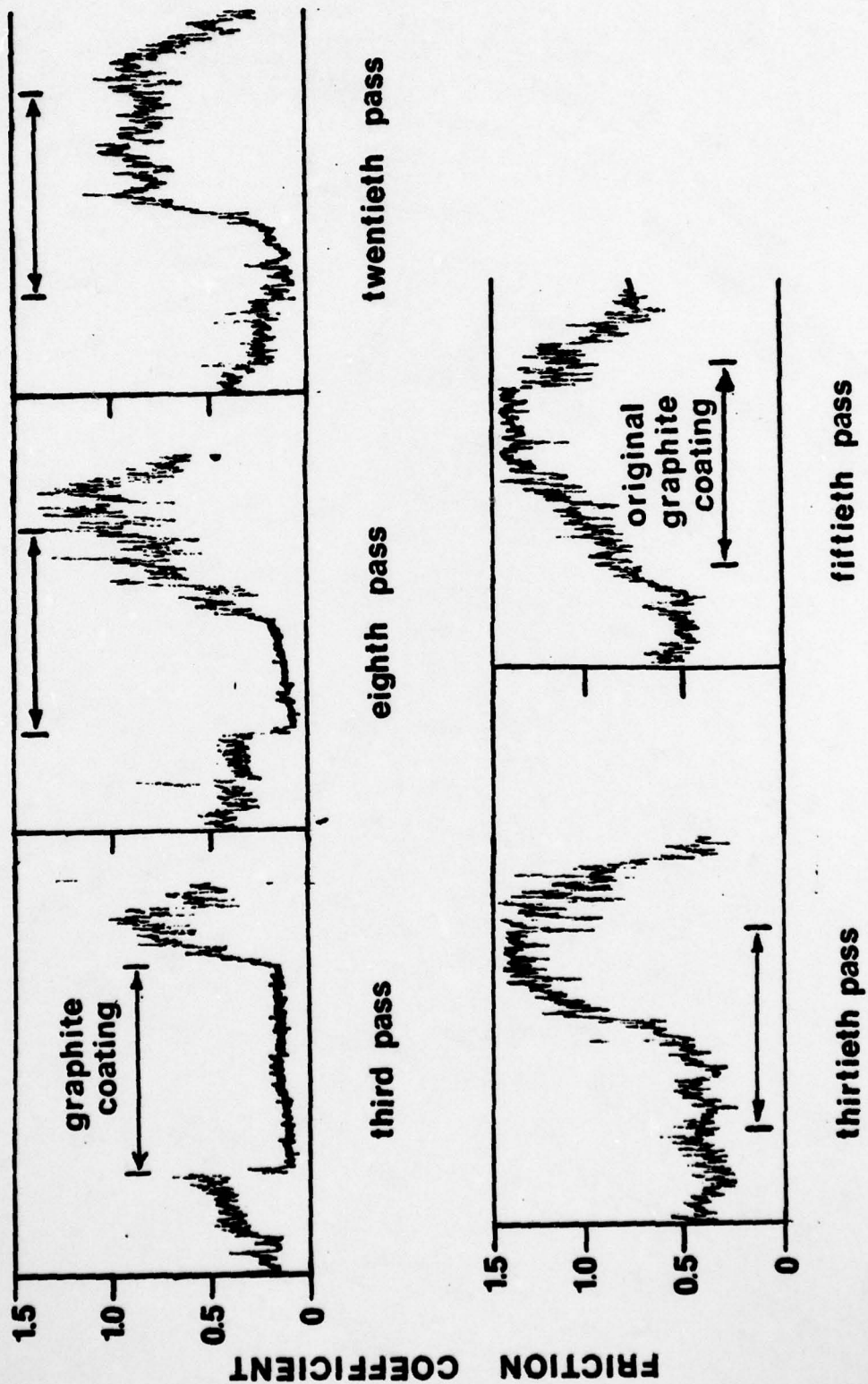


Figure 38 - Friction coefficient versus position for partially graphite coated aluminum during test shown in figure 37 on five different passes (leads EE trace by approximately  $90^\circ$ ).

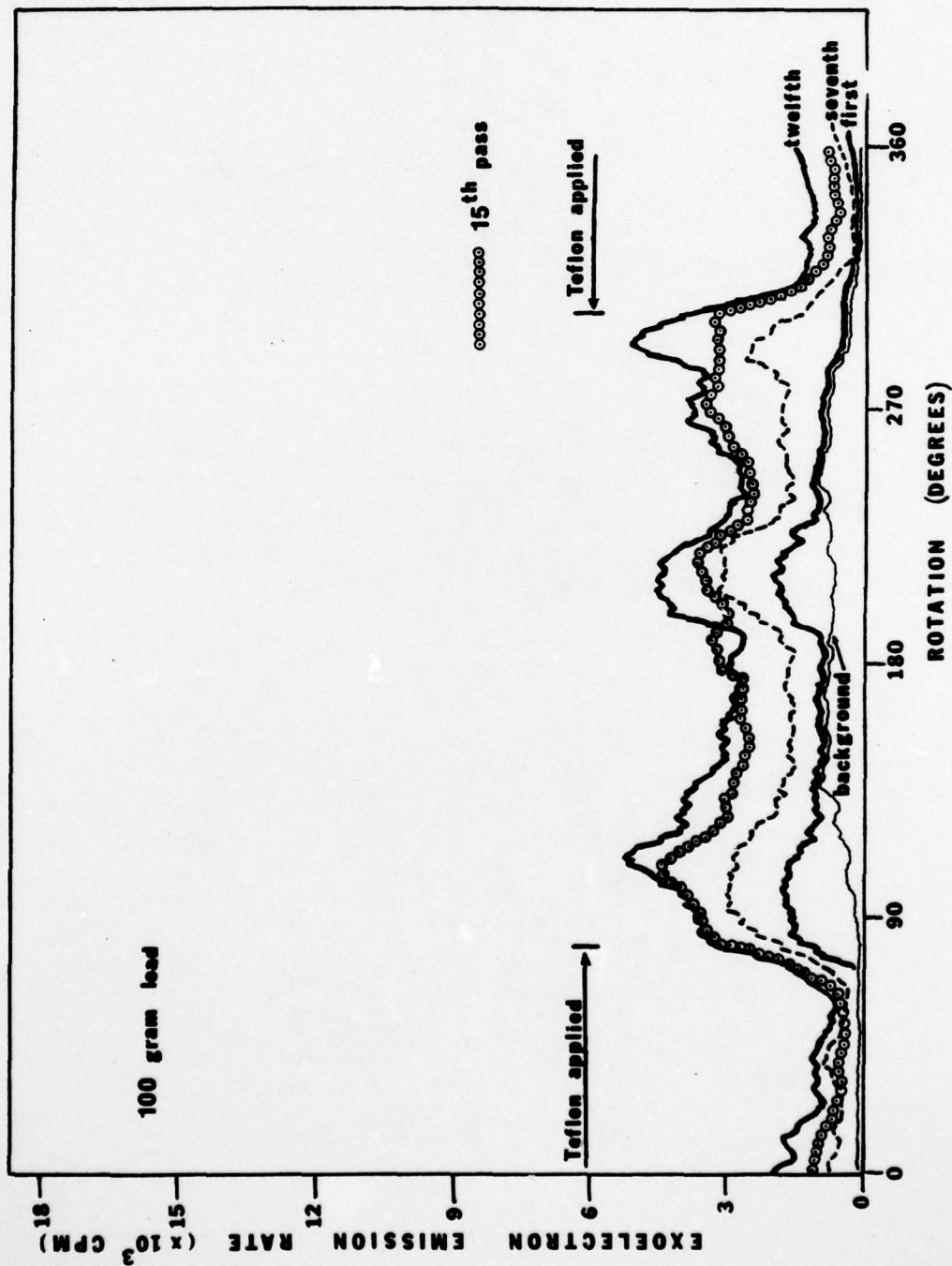


Figure 39 - EE from partially Teflon coated aluminum during simultaneous wear test at 100 grams with 52100 steel pin.



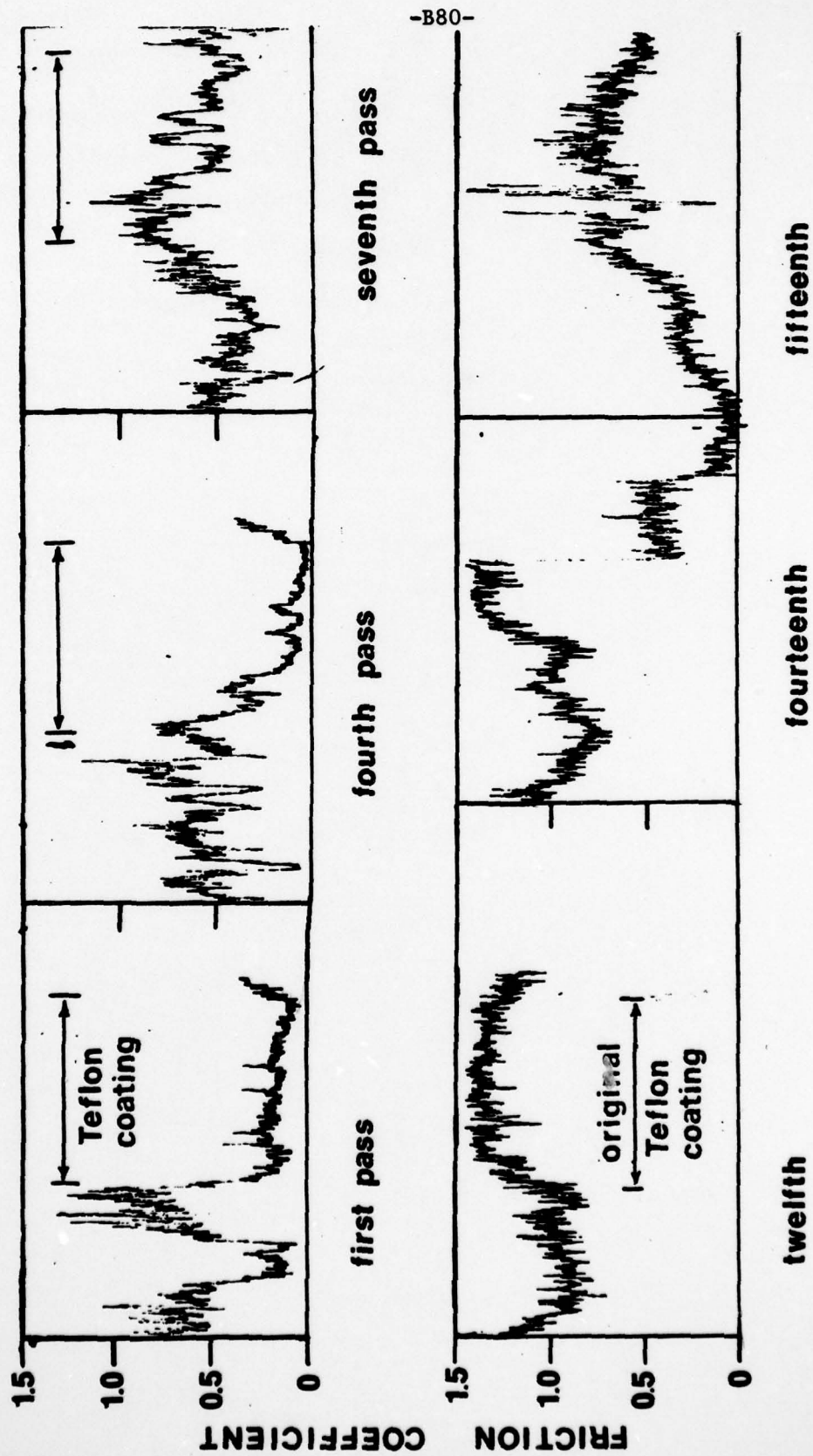


Figure 40 - Friction coefficient versus position for partially Teflon coated aluminum during test shown in figure 39 on six different passes (leads EE trace by approximately  $90^\circ$ ).

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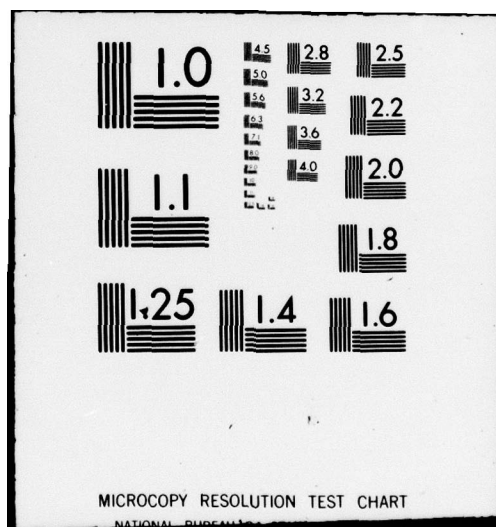
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#### 5.4 Discussion

As expected, the lower pressures at which these wear tests were conducted, did influence the exoelectron emission somewhat. Referring to figure 33, it can be seen that wear tests conducted in a vacuum of  $10^{-5}$  torr produce anywhere from the same to one-half the rate of EE obtained if that same test was run at atmospheric pressure. The reasons why the emission only increased over the central portion of the wear track is unclear - perhaps it might be due to slight differences in the adsorption of water and oxygen molecules along the track. Nevertheless, although possibly fewer in number, exoelectrons are still readily detectable at  $10^{-5}$  torr. It is recommended, however, that any future simultaneous wear tests not go much below the pressures used here.

The fact that emission increased slowly, finally reaching an apparent maximum and staying there no matter how many more revolutions took place, has an obvious explanation. The rate of formation of new surface area is of course greatest on the very first pass and apparently the rate becomes minimal after many revolutions. All of this is mirrored in the rate of EE growth.

The question of solid lubricant migration is a tricky one to address. Obviously, we were unable to test all possible combinations of load, speed, coating thicknesses, different methods of application, different pin and substrate materials etc. For the limited number of tests that were conducted it seems safe to conclude that graphite and molybdenum disulfide are removed monotonically. If migration were to occur at all on a specimen which was half covered with lubricant (that

is, the pin, starting at  $0^\circ$  travels  $180^\circ$  on a bare aluminum surface and then goes through the next  $180^\circ$  on the coating), one would expect the lubricant to migrate in the same direction that the pin moves. After several revolutions the wear track might be bare from  $10^\circ$  through  $190^\circ$ , and then be covered with lubricant from  $190^\circ$  (back through  $0^\circ$ ) to the  $10^\circ$  mark. This however was not observed with either the  $\text{MoS}_2$  or graphite used in these tests. The friction and EE scans indicated first removal to be on the fringes of the coated area, with the center portion of the coated track the last to be stripped bare. This, it is believed, is due to the orientation of the film in relation to the wear track. The lubricants were usually rubbed on (over the semi-circular area) in a back and forth motion, parallel to an imaginary line corresponding to clock hands in the six o'clock position. The motion of the pin, therefore, is perpendicular to the film orientation at "twelve" and "six o'clock" but parallel to the film orientation at the "three o'clock" position. Since the film doesn't have to reorientate itself at the "three o'clock" position, this center portion of the coated wear track is the last to become bare.

Perhaps the single most important variable which might affect migration (if it is to occur) would be the real area of contact the pin or rider makes. With powder type coatings, if the area of contact is too small there may be no room for the powder particle to adhere to the pin. In the end, therefore, the pin ends up scratching through the coating.

Obviously with the Teflon coatings migration can occur, as was shown in the previous chapter. In the test presented in this chapter,

however, it is believed that the reason for the sudden decrease in both friction and EE during the 15th revolution was not due to migration, but rather, a slight shift of the pin. Notice that although the friction decreases to a value for Teflon on Teflon, the EE decreases, but not totally. Therefore, since the "old" wear track was still emitting exoelectrons, we see the friction approach zero, but not the EE.



## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

The exoelectron emission process is a successful semidestructive tool for detecting localized film failure due to wear and in the study of the migration of solid film lubricants. The process can tell us little about the coating per se, although, it does reflect conditions at the coating-substrate interface. It is mainly for this reason that EE fails as a tool for predicting hard coating quality and the premature failure of these coatings. EE might be used in the factory if the time lag between grit blasting the substrate and application of the coating is not too great. In this manner, defects would not have to penetrate through the metal - just up to the interface would suffice, since after sandblasting the base metal is still "fresh." Of course, there were cases in which EE located premature defects due either to wear or to grinding. Also, it should be remembered that at no time were we able to locate cracks through to the metal by other means and not have a corresponding indication from the exoelectron emission. However, we feel unjustified in making any claims that the emission of exoelectrons (a substrate phenomenon) can always locate cracks in the coating or predict its quality.

Exoelectrons are an ideal tool in locating those areas where the film has worn away. Provided that we have a substrate and a coating which undergo different rates of EE, one will always be able to locate those spots where the coating is gone. If visual or friction measure-

ments are difficult or impossible, as they often are, EE is the logical alternative to monitor the film. It has the advantages of looking at much larger areas in finer detail and the ability to be carried out either during or after a wear test.

The simultaneous wear/friction/EE tests are a more logical way to study the processes involved than the "static" EE tests. These tests showed that, under the conditions we employed, graphite and  $\text{MoS}_2$  wear monotonically - that is once the substrate is exposed, lubricant will never move to cover it over again. The orientation of the film in relation to the direction the pin moves, plays an important role in determining how long the film will last.

Teflon was found to migrate, but only under certain conditions which depended on the method of application and the preparation of the substrate. The movement, when it did occur, was over very small distances, on the order of a millimeter. Only films which were baked on exhibited migration - those which were rubbed on did not.

## 6.2 Recommendations

The first recommendation is that the method of detecting exoelectrons be changed. It is felt that the construction of a device to measure EE in air is warranted. Hoenig (16) has demonstrated that this detection method is feasible and, of course, more viable for real-world applications. In this way, we would not be subject to attacks claiming our methods of testing are only good as a research tool.

Additional tests with the wear resistant coatings seem pointless unless they are done simultaneously. However, present load limits of



the newly constructed apparatus would not be conducive to promoting cracks or wearing the film away quickly.

Solid film lubricants seem best suited for further tests in the vacuum chamber. Different combinations of load, speed, methods of coating application, coating thickness, pin and substrate materials need to be examined before any claims regarding migration can be made. Of course if we would test these films in air, the additional variable of pressure could be included.

As with most new materials research methods, exoelectrons are not without their problems. A common difficulty seen throughout most studies is one of cleanliness. Should anything come between the fresh metal surface and the detector, the electrons (which have very little energy to begin with) usually are absorbed by this "foreign" material. Perhaps a solution lies within the problem itself - that is, exoelectrons might be best if employed as a determination of surface cleanliness.

When it comes to material degradation, exoelectrons can only be used when the conditions are right. Therefore, it seems that, for now, they will remain in the research laboratory (rather than the factory) where conditions can be closely monitored.

The other problem is a better understanding of the process itself. Perhaps this is something we (engineers) should let the physicists deal with. Almost every paper dealing with exoelectrons ends on this same note - that is, even though we are using exoelectrons, everyone would feel more comfortable if they knew the exact set of conditions necessary for their emission.



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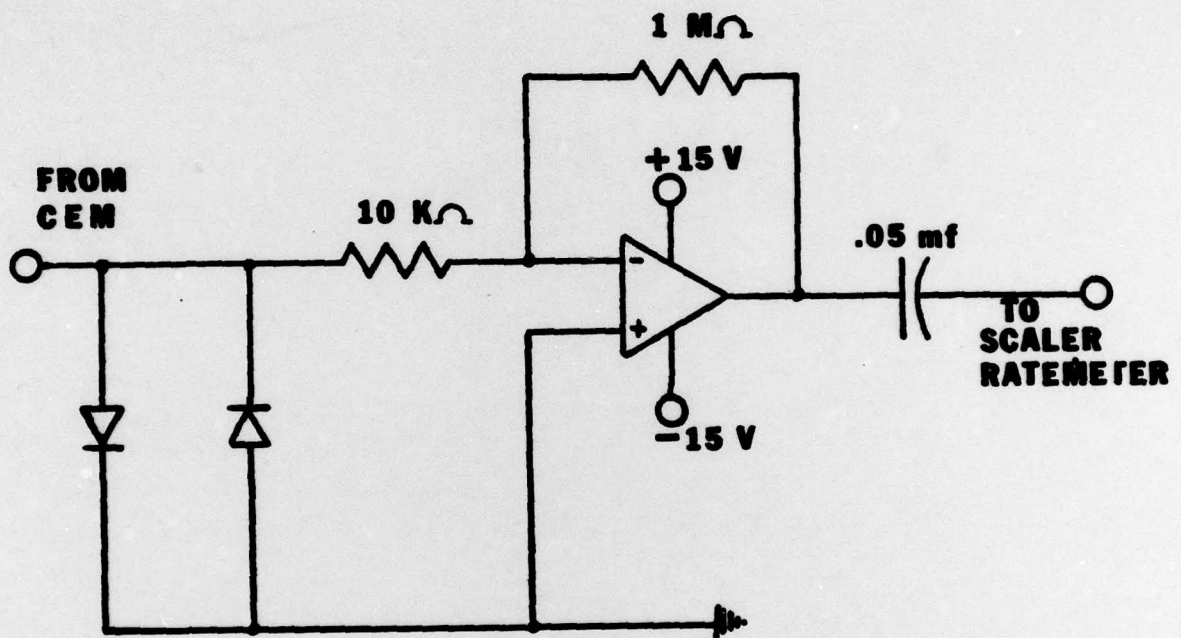
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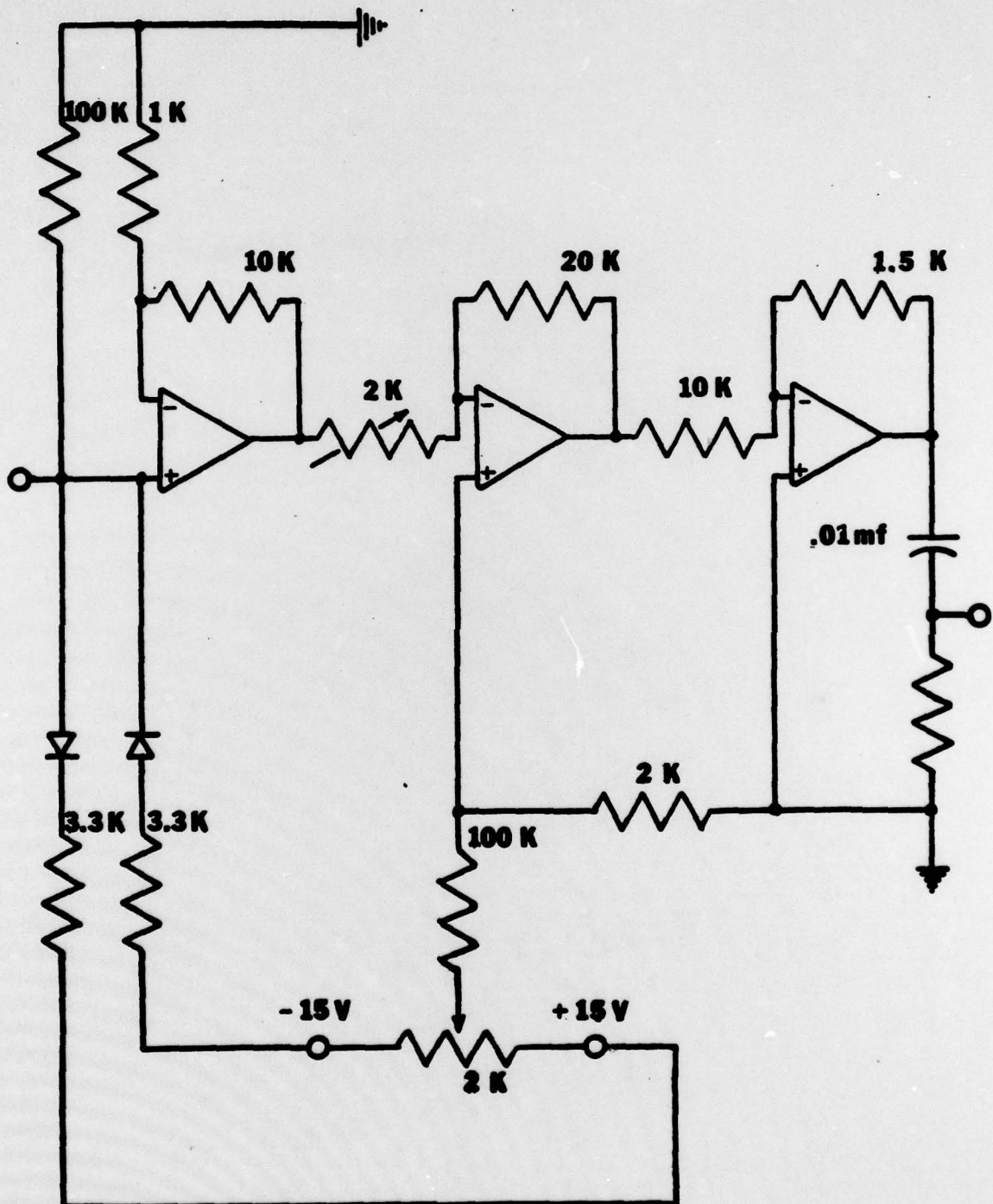
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Appendix 1A - Present amplifier circuitry

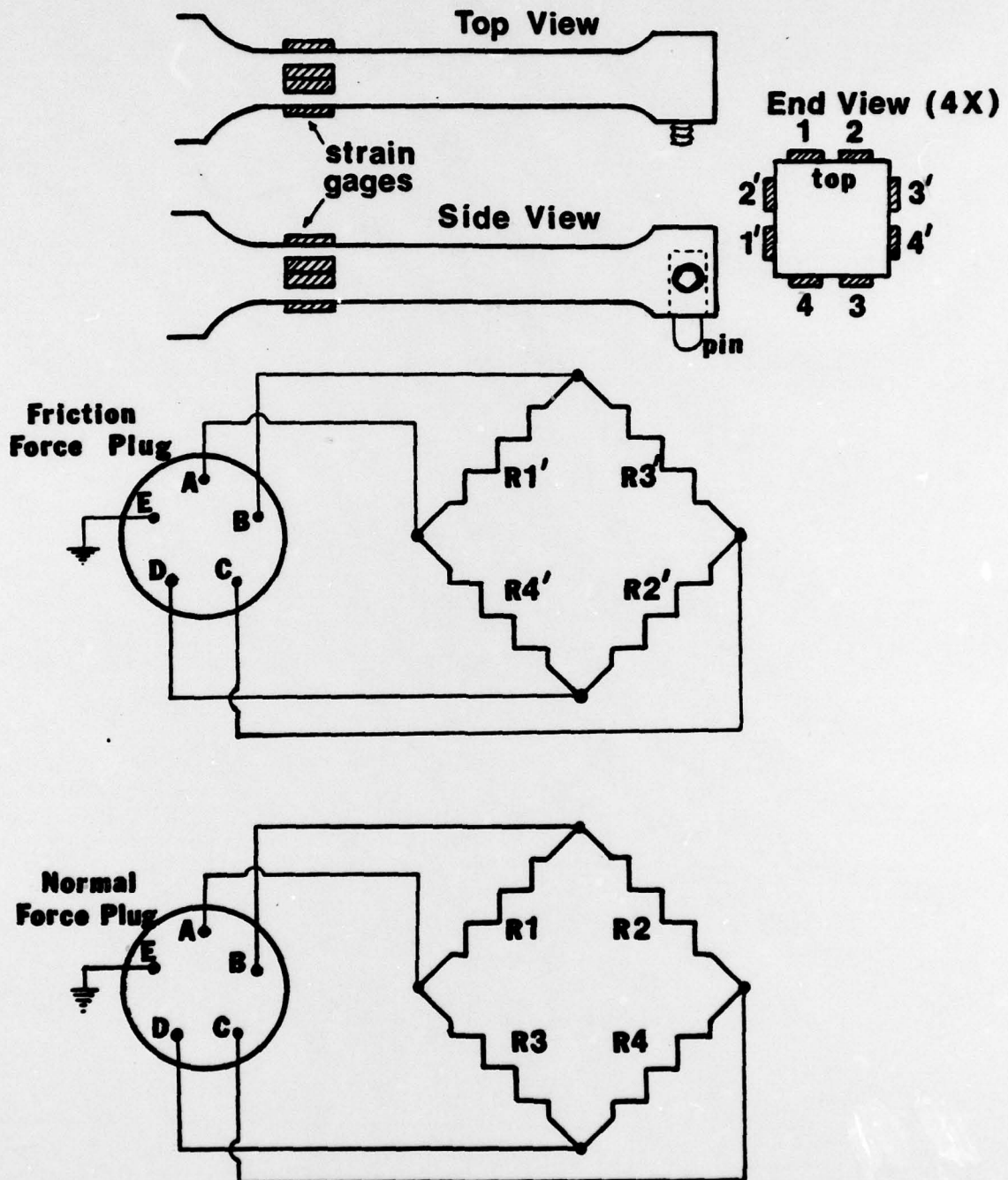
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Appendix 1B - Previous amplifier circuitry (from reference 17).

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# **Cantilever Beam Load Cell** (drawn 2X)



Appendix 2A - Configuration of load cell used in vacuum chamber and plug connections.



E = Young's modulus,  $10 \times 10^6$  psi

b = beam width, 0.172 inches

h = beam height, 0.172 inches

l = beam length, 1.345 inches

I = moment of inertia  $7.27 \times 10^{-5}$  inches<sup>4</sup>

L = distance from center of gages to center of pin, 1.030 inches

P = force at pin in pounds

The strain at the gages is:

$$= \frac{6PL}{Ebh^2}$$

Appendix 2B - Values for the aluminum cantilever beam load cell in appendix 2A.

<u>Coating</u>	<u>Method of Application</u>	<u>Composition (weight %)</u>	<u>Bond Strength (psi)</u>	<u>Hardness kg/mm<sup>2</sup></u>
Rokide ZS	flame spray	ZrO <sub>2</sub> (64%) SiO <sub>2</sub> (33%)	600-1000	890
Union Carbide LA-7	D-gun	Al <sub>2</sub> O <sub>3</sub> (60%) TiO <sub>2</sub> (40%)	9000	950
Union Carbide LC-4	Plasma-arc	Cr <sub>2</sub> O <sub>3</sub> (99%)	8000	1300
Union Carbide LW-1N30	D-gun	WC (88%) Co (12%)	25000	1300

Appendix 3 - Wear resistant coatings and properties.

### Appendix C - Additional Tests

The final month of the project involved additional "simultaneous" tests on the solid lubricant, teflon. Lighter loads, different methods of application and different substrates were examined. In each case, the same pin (52100 steel), the same speed (1 cm/min @ 1 rpm) and the same pressure ( $10^{-5}$  torr) were employed. Again, we were specifically looking for any possible migration which might occur along the wear track. Each specimen we dealt with was only half covered with lubricant (semi-circular area) while the other half was bare metal substrate.

With lighter loads, no migration was observed with pure teflon rubbed onto an aluminum substrate. Loads of fifty and seventy-five grams (versus the 100 grams used in previous tests) produced the typical behavior of a gradual increase in EE on the uncoated section, and an eventual increase on the coated portion. No decrease in EE was noted at any time during the tests, and likewise, friction force measurements showed that no movement of the teflon was taking place.

A commercially applied teflon coating, known as S-#550, and purchased from the American Durafilm Company, produced some very interesting results. This coating had a thickness of 2 mils (on a steel substrate) and is used primarily for its abrasion resistance. Because of the excellent wear resistance of the coating, a high normal load of 500 grams was applied to the pin. At first, typical results were obtained from the exoelectron emission as seen in the accompanying figure (1st, 5th, and 10th revolutions). The friction force, also, was generally as expected for the initial revolutions, except for the very first revolution which showed a fairly low value for



steel on steel (see accompanying figure). However, by the 10th revolution, the friction was off scale, as would be expected for steel on steel in a moderate vacuum ( $f$  usually  $\sim 1.0$ ). By the 50th revolution, the friction had dropped slightly for the steel pin on the teflon coating indicating that by this time, the teflon along the wear track had become "orientated." More importantly, however, is the fact that the friction coefficient on the uncoated steel was beginning to drop. Obviously, some transfer of teflon was taking place (or migration). This was verified by the 60th EE trace which showed a significant decrease in the overall emission rate from the uncoated steel section. Subsequent revolutions showed steady decreases in both the friction and EE on the uncoated portion. Examination of the wear track after the last (600th) revolution, via an optical microscope, demonstrated that teflon was indeed present on that portion of the wear track which originally consisted of uncoated steel. Although the width of the transferred layer varied, it was present over the entire  $180^\circ$  (as seen both optically and by the EE).

Obviously the transfer (or migration) of the teflon was quite evident on this last test with teflon S-550. Migration occurs not because a different substrate was used (steel instead of aluminum) but because of the different method of application, the higher thickness, and the different type of teflon.

Further study of migrating film and their potential as exceptionally effective solid film lubricants is in order.

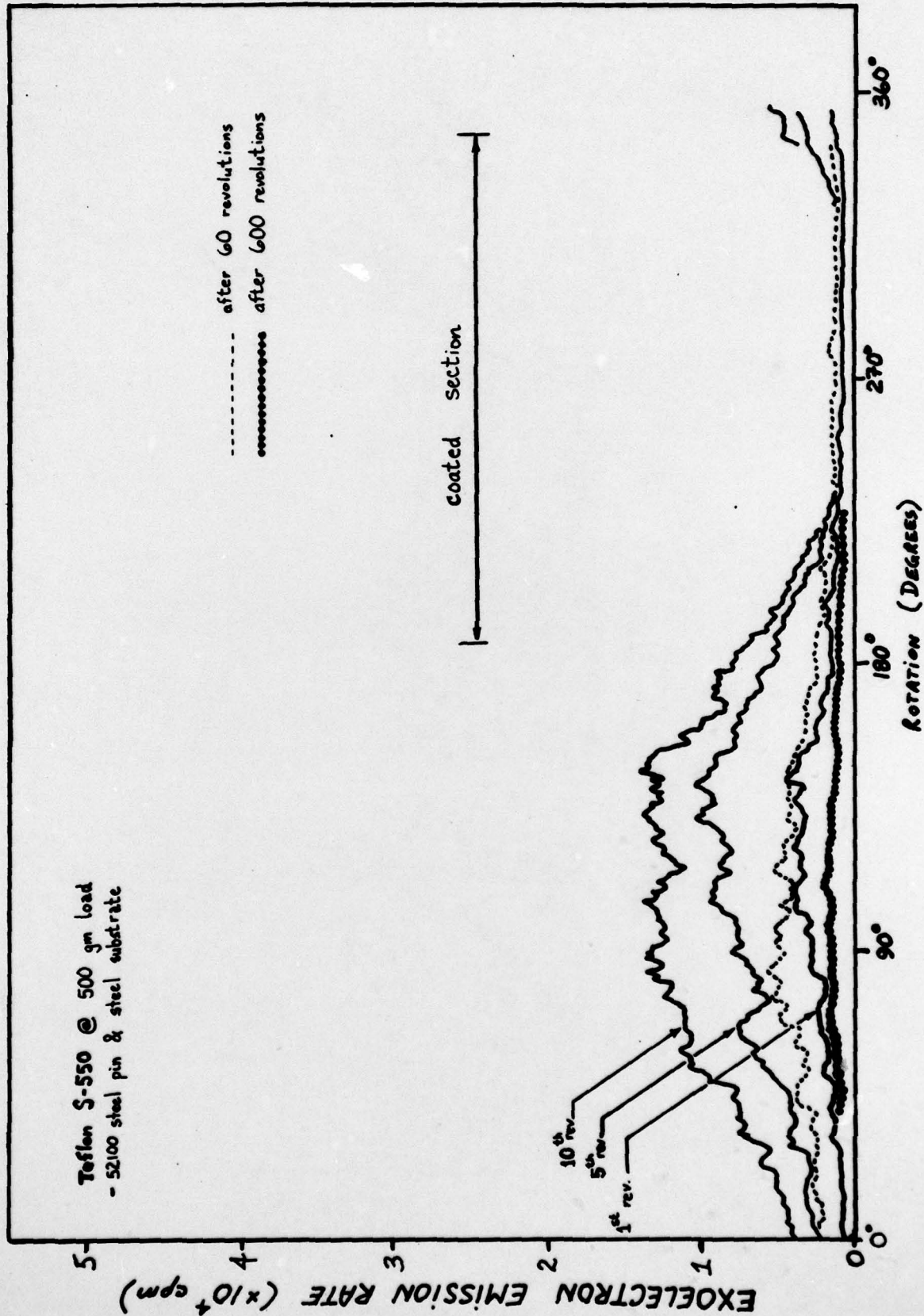
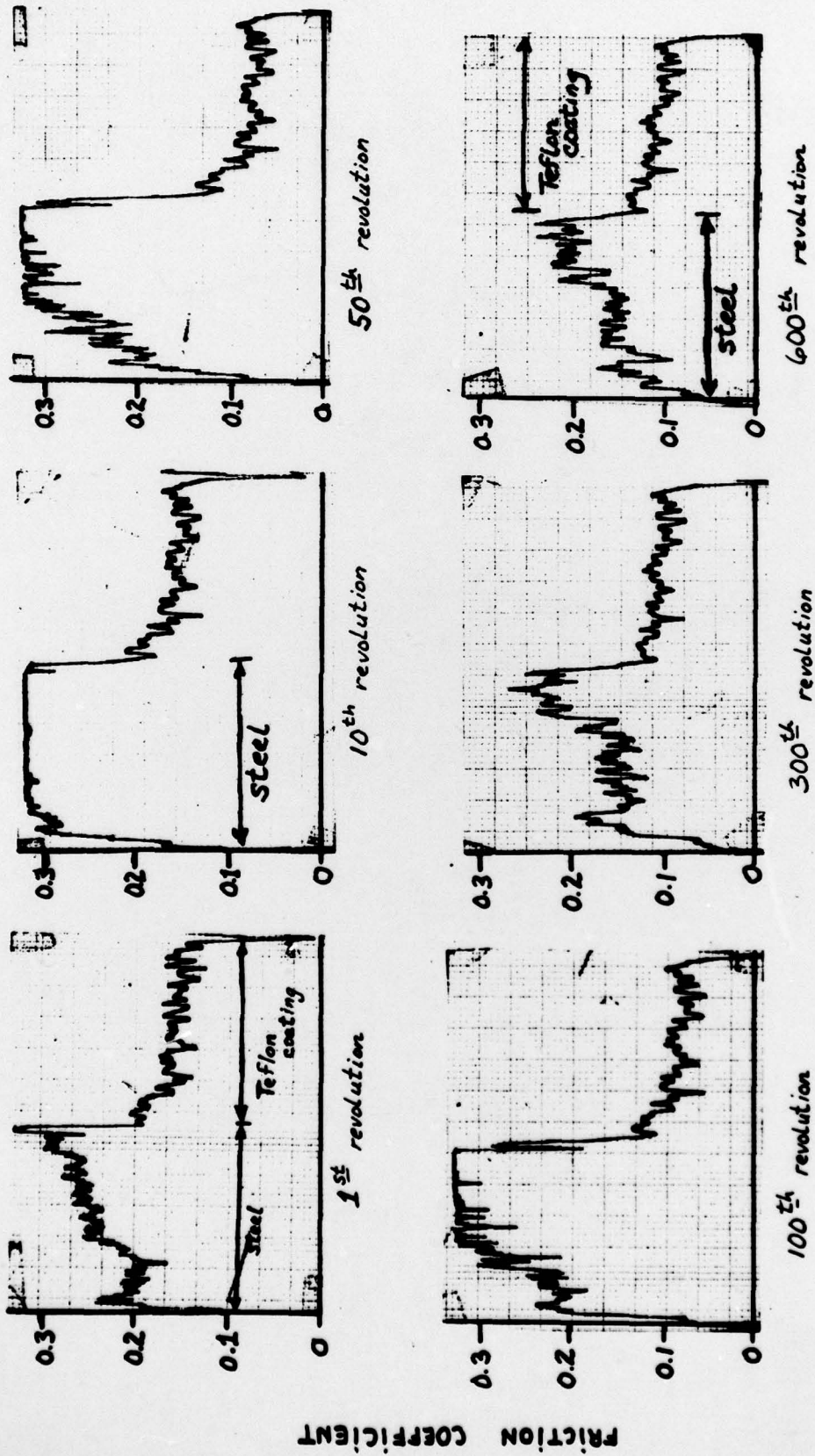


Figure C-1. Exoelectron emission as a function of angle of rotation, for a Teflon S-550 film being worn by a steel pin. Note that between 10 and 600 revolutions there is a drastic reduction in emission in the (initially) uncoated section of the wear track.





Teflon S-550 @ 500 gms load 52100 steel pin and steel substrate.

Figure C-2. Friction coefficient as a function of angle of rotation for a steel surface partially coated by Teflon S-550. The friction of the uncoated section (labelled 'steel' in the figure) reaches a maximum after 10 revolutions and then starts to drop, as teflon covers part of the wear track.